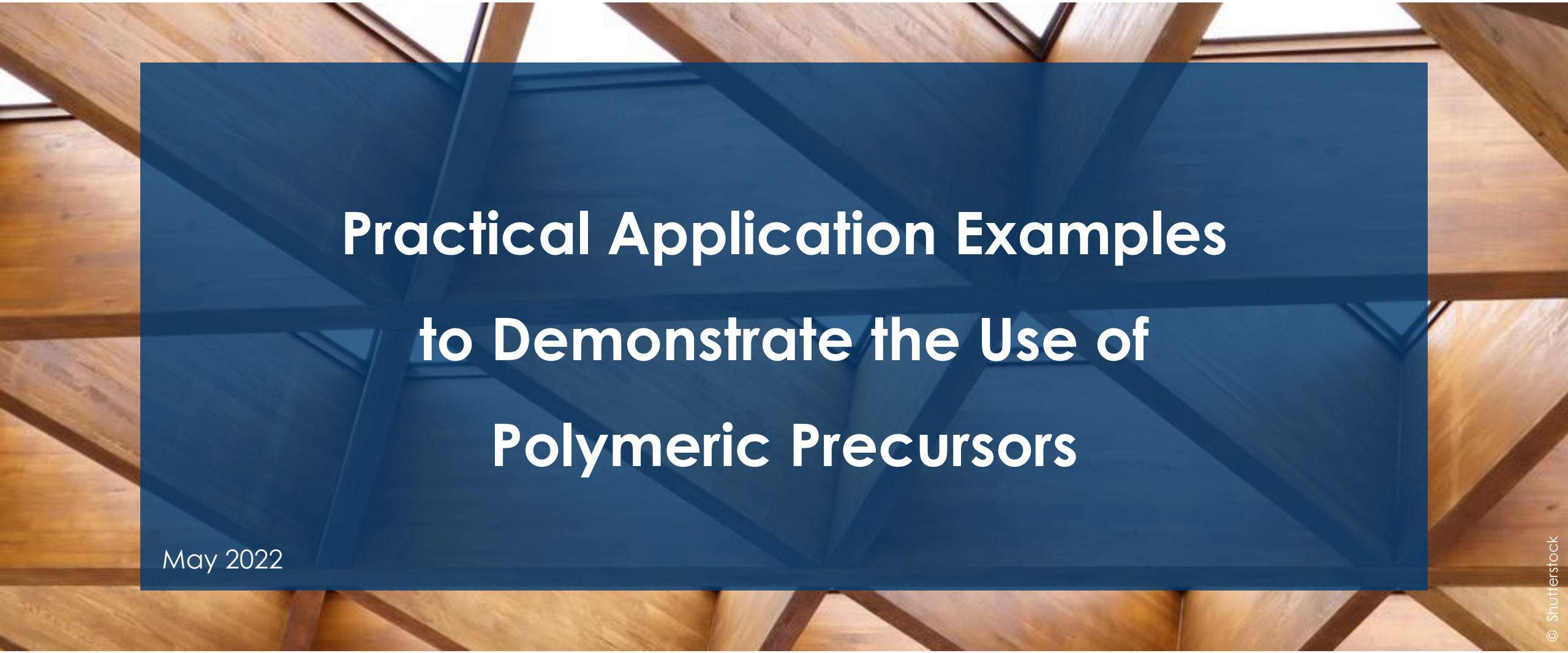
FEICA®

The European voice of the **adhesive and sealant industry**



Practical Application Examples to Demonstrate the Use of Polymeric Precursors

May 2022

Introduction

- The aim of this presentation is to demonstrate by giving practical examples that polymeric precursors **can be safely handled** under **adequately controlled conditions** without causing harm to humans or the environment

- FEICA would like to provide four examples:
  1. One-Component Foam (OCF) - Industrial + Professional
  2. Direct Glazing (windshield bonding for cars) – Industrial + Professional
  3. Lamination of flexible substrates with reactive polyurethane (PU) adhesives – Industrial
  4. Liquid 2-component silicones for gasketing - Industrial

Customisation of Polymers

- Customised polymers are common throughout the adhesives and sealants industry.
- Customising refers to modifying existing polymers to satisfy certain needs and to manufacturing unique polymers for specific applications
- The composition of reactive polyurethane adhesives addresses specific processing and performance requirements of very different application areas, e.g.
  - Improved efficiency in production, e.g. faster line speed in assembly lines
  - Lower application temperatures to reduce energy consumption
  - New substrate combinations including recycled & bio-based materials
  - New design of the assembled part, e.g. lightweight, designed for recycling
  - More demanding properties in end-use
  - Support of the Green Deal initiative of the Commission and UN Sustainable Development Goals (SDGs)

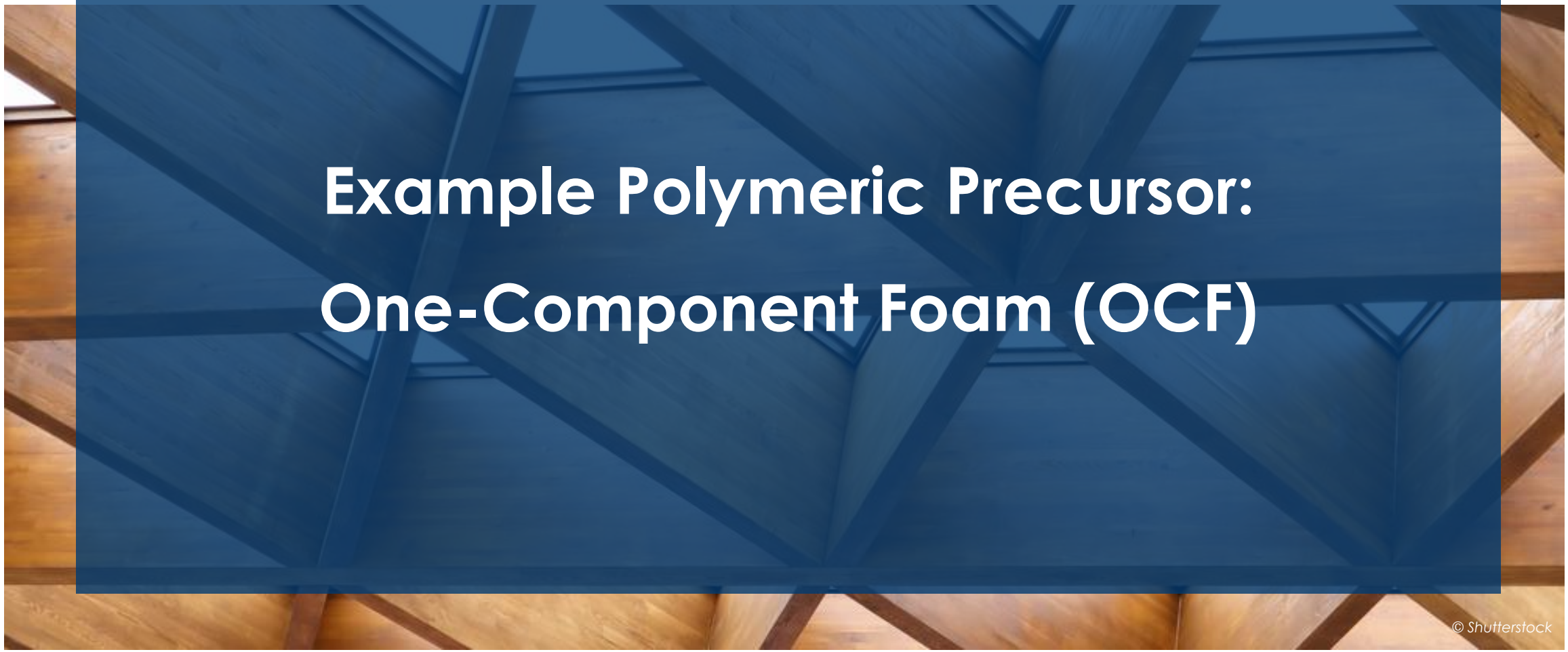
Customisation and continuous improvement of PU-adhesives are key to help our customers to stay competitive and respond to a changing market requirements

Adhesives Supplier Landscape

- **The adhesives industry is mainly structured around SMEs** plus a few multinational operating companies
- **In-house polymerisation** is common across the adhesives industry to meet the **demand for tailor-made products in a timely manner** across multiple application areas
- **There are many thousands of different polymer precursors** with a molecular weight number average < 10,000 Da
- **Each individual polymer precursor is almost exclusively from one supplier**
- **Not only would thousands of polymers would need to be registered, but also thousands of different registrants would be involved**

Innovation in a dynamic market is key for SMEs and larger adhesive suppliers to stay competitive.

Example Polymeric Precursor: One-Component Foam (OCF)



Introduction

- One-component foam (OCF) is based on polyurethane chemistry and is the generic term for moisture-curing one-component foams dispensed from pressurised containers
- OCF brings significant benefits to window and door installation tasks
- OCFs connects, provides thermal and acoustic insulation and renders joints airtight
- OCF plays an important role in this context by improving energy efficiency and helping create a more pleasant environment

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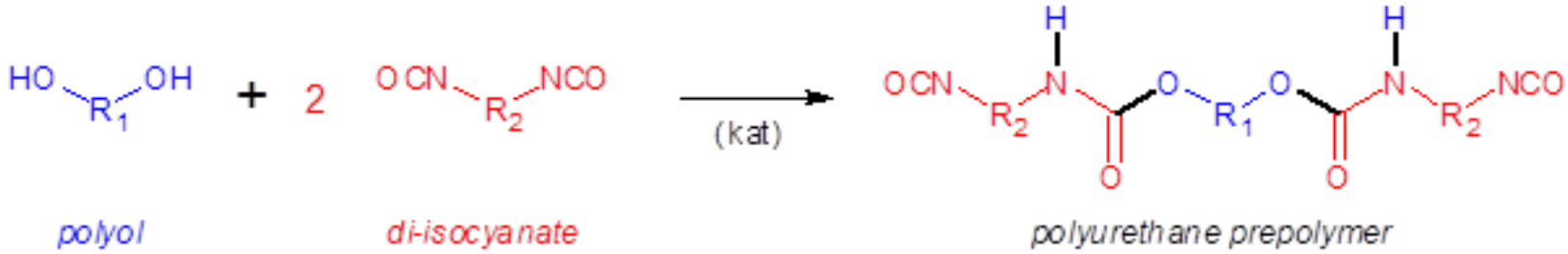
Industrial step - Production of a polymeric precursor

Chemistry

To make one-component polyurethane foam, you need two main chemical ingredients, namely polyol (which is also a polymeric precursor) and diisocyanate. These chemicals form the building blocks of polyurethane. When polyol and diisocyanate react, they form a polyurethane prepolymer, also called a polyurethane precursor.



Industrial step - Production of a polymeric precursor

Production of polymeric precursor

The manufacturing process of a polyurethane precursor is carried out in a predominantly closed system. Polyol and diisocyanate arrive in bulk. Via a special chemical unloading dock, with provisions to collect potential spillage, the raw materials are unloaded into large tanks.

Industrial step - Production of a polymeric precursor

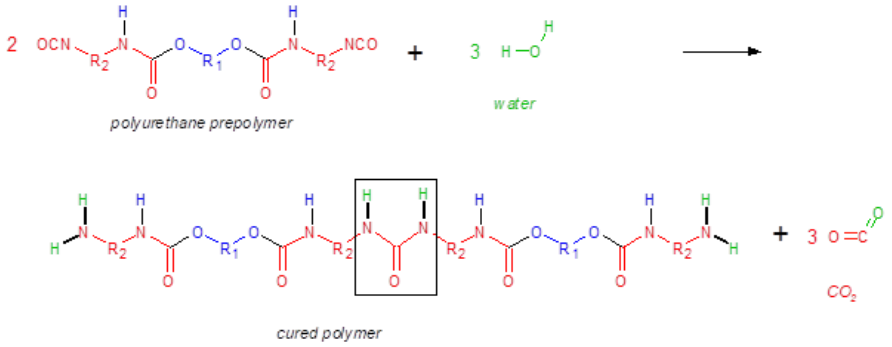
- Next, the polyols and diisocyanates are mixed in a can under pressure, and the polyurethane precursor is formed. Thanks to this closed process, cleaning steps are not required and the raw materials do not come into contact with the environment.

- Further, it is important to note that the formulation process for a polyurethane precursor is highly water sensitive due to the reactivity with isocyanates used in product formulations. No part of the formulation process is in contact with water and, therefore, no part presents a potential for environmental exposures.

Professional step - Application of a polymer precursor

Chemistry

During use, this precursor, present in the OCF can, is dispelled under pressure as a viscous foam gel that solidifies by reacting quickly with moisture in the atmosphere to form a chemically and physically stable and rigid polymer foam product.



polymeric precursor
= polyurethane prepolymer

H_2O

Professional step - Application of a polymer precursor

Application of a polymeric precursor

- During application the polymeric precursor is extruded from the can and forms a viscous foam gel that solidifies by reacting quickly with moisture in the atmosphere to form a chemically and physically stable and rigid polymer foam product. This is called the curing step

- The curing times for OCF are typically within minutes of use for the initial cure. Higher atmospheric humidity can result in faster cure times:
  - Tack free time (initial curing): < 10 minutes
  - Cutting time (OCF can be cut): < 1 hour

  The extruded foam is not touched until it is fully cured.

Professional step - Application of a polymer precursor

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Application by a professional worker of OCF, containing the polyurethane precursor, in a window frame

Description of use, exposure and waste management

OCF is used in a variety of applications in the building and construction sectors, for example, to fill gaps in building walls. OCF contributes significantly to heat gain of the building. This is an important factor for overall building energy efficiency.

The polyurethane precursor is used when door and window frames are installed. There is no direct contact by the professional worker. During use of the polyurethane precursor, the professional worker takes into account the necessary safety measures and wears the required personal protective equipment (PPE), in accordance with the risk analysis of the mixture and the unreacted monomers, which have a more significant hazard profile compared to that of the polymeric precursor

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Description of use, exposure and waste management

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After application, these products are always covered by, for example, doorframes, window frames or plaster. They are used exclusively on the inner shell of buildings, and contact with the outside environment will not take place. Excess foam will be removed by cutting it with a sharp knife after the foam has cured, so no contact with the polymeric precursor takes place.

Classification

- The one-component foam carries the following hazard sentences:

Aerosol, Category 1	H222; H229
Acute toxicity, Category 4	H332
Skin corrosion/irritation, Category 2	H315
Serious eye damage/eye irritation, Category 2	H319
Respiratory sensitisation, Category 1	H334
Skin sensitisation, Category 1	H317
Carcinogenicity, Category 2	H351
Specific target organ toxicity — Single exposure, Category 3, Respiratory tract irritation	H335
Specific target organ toxicity — Repeated exposure, Category 2	H373

- These phrases result from residual monomeric isocyanate in the sample; the polymeric precursor does not influence this classification
- Risk management measures are listed on the Safety Data Sheet (SDS)
- The hazard results from the monomeric isocyanates of the polyurethane foam. As there is an application step involved, strictly controlled conditions are not possible.

Example: Direct Glazing (Industrial and Professional)

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Direct Glazing

- **Direct glazing** means the bonding of automotive window panels with a suitable adhesive directly to the car body
- Direct glazing is used both for
  - **installing windows at the manufacturing line** of the car producer (an **industrial** application) as well as for
  - **replacing car windows** after damage (a **professional** application)
- Both examples will be discussed in this presentation
- The direct glazing adhesives discussed in this presentation are based on **polyurethane chemistry**. Details will be shown on the next slide
- The aim of this presentation is to demonstrate that direct glazing adhesives **can be safely handled** under **adequately controlled conditions** without causing harm to humans or the environment

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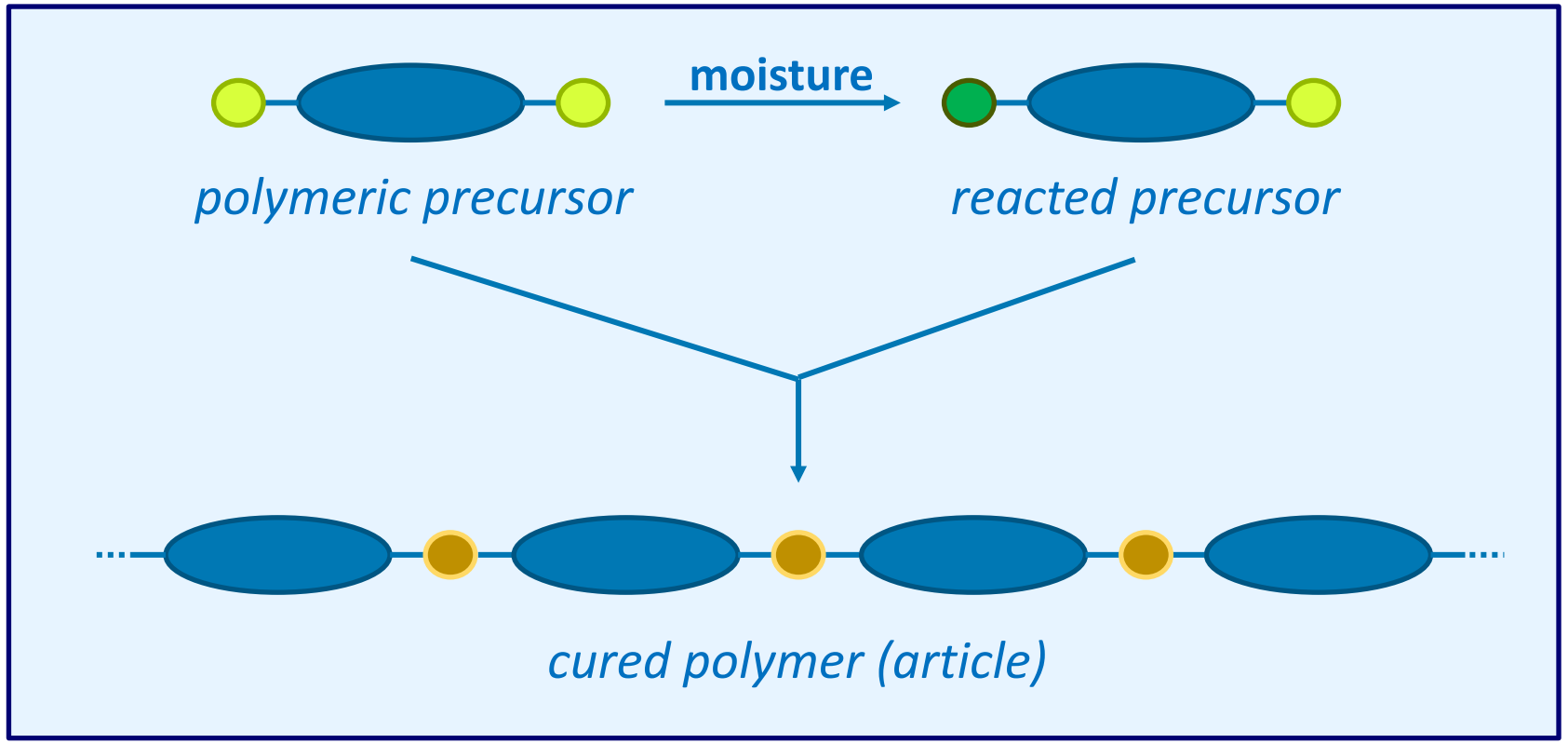
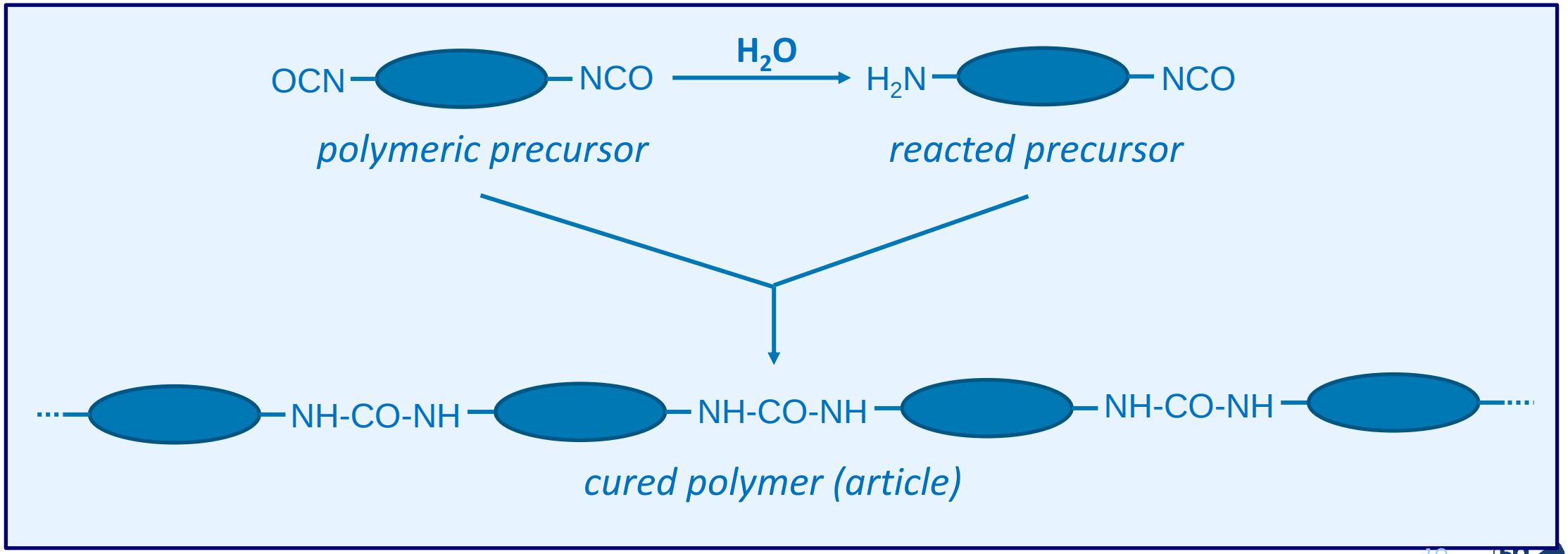
Curing Chemistry

One-component polyurethane chemistry is a chemistry based on **isocyanate-functional polymers** (*polymeric precursors*) which can react with ambient moisture. Isocyanate groups converted by moisture can further react with unreacted isocyanate groups to form the cured polymer (article; often a cross-linked network).



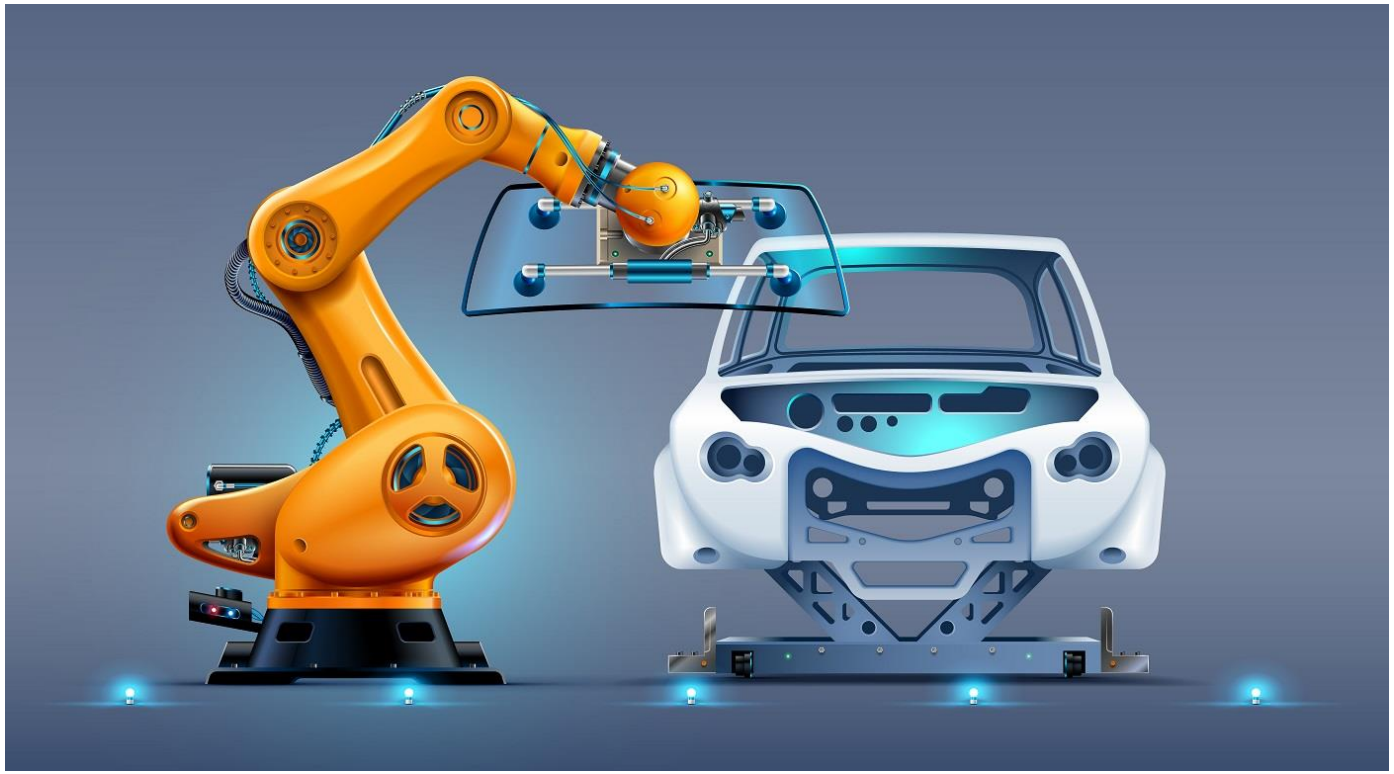
Curing Chemistry II

One-component polyurethane chemistry is a chemistry based on **isocyanate-functional polymers** (*polymeric precursors*) which can react with ambient moisture. Isocyanate groups converted by moisture can further react with unreacted isocyanate groups to form the cured polymer (article; often a cross-linked network).



Automated Windshield Installation (Industrial)

The entire application process is controlled by automated application equipment (robots) without any workers being present



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Automated Windshield Installation (Industrial)

The adhesive is delivered out of a drum in an automatic dispensing station and pumped directly to the application robot

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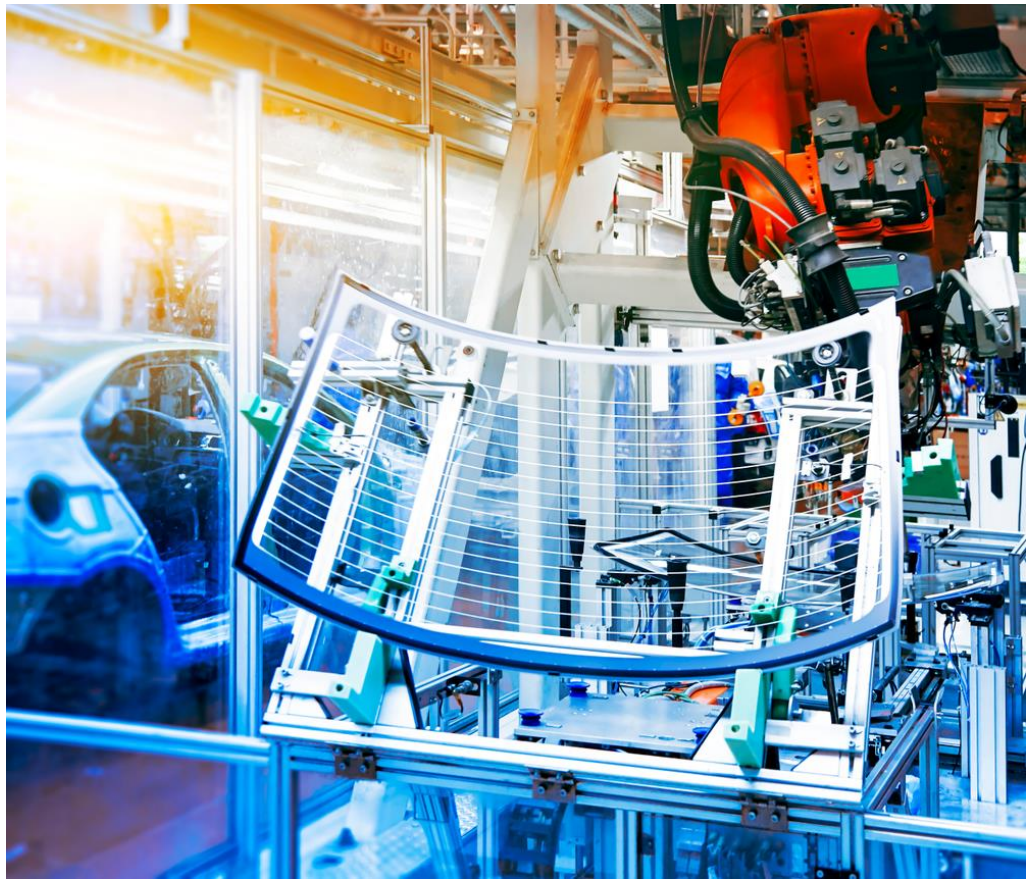
Automated Windshield Installation (Industrial)

The windshield is then fitted into the car, typically also by a robot



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Windshield Installation (Industrial)

- The adhesive for industrial applications is delivered in drums fitted with inliner bags. These prevent the drums and other equipment from coming into contact with the adhesive.
- The adhesive is pumped from an automatic drum press to the automated application equipment. Except for changing drums no interference of workers is necessary.
- Drums are changed by trained teams of professionals, who accomplish changing the drums in a minimum amount of time (10 – 15 min.) without any waste or spills. Protective equipment is worn. Because the adhesive is pastelike and cures into a solid, cross-linked material, there is no discharge of the polymeric precursor into the environment.
- The inliner bag is taken from the drum. Residual adhesive still adhering to the inliner will cure into a solid, cross-linked polymer after coming into contact with air. It can be disposed of together with the inliner bag as regular waste. The drum will be recycled.
- Two trained professionals will spend approximately 1 hour per day with changing drums (2 application stations per line; 2 drums per station and day). During the application process itself (robotic) no workers are involved.

Windshield Installation (Industrial)

Classification:

- The adhesive carries an H317 phrase (*May cause an allergic skin reaction*) and a H334 phrase (*May cause allergy or asthma symptoms of breathing difficulties if inhaled*)
- Both phrases are driven by residual monomeric isocyanate in the sample; the polymeric precursor does not influence this classification
- Risk management measures are listed in the SDS:
  - P261 Avoid breathing dust/fumes/gas/mist/vapours/spray
  - P280 Wear protective gloves/protective clothing/eye protection/face protection/hearing protection/
  - P284 [In case of inadequate ventilation] wear respiratory protection
- The hazard is driven by the monomeric isocyanates of the adhesive. As there is an application step involved, strictly controlled conditions are not possible

Windshield Installation (Industrial)

Application videos

- Application of the direct glazing adhesive:

  DIRECT GLAZING – YouTube

- Installation of the windshield:

  Car Windshield Assembly by Robots

Windshield Replacement (Professional)

- Damaged windshields need to be replaced. This is typically done in a professional glass repair shop, in a car repair shop or by a mobile repair team at the location of the car (e. g. parking lot)
- The adhesive is manually applied from an adhesive gun by a trained professional
- After application of the adhesive, the windshield is fitted by the professionals into the car body
- The adhesive is then left to fully cure, either in the repair shop or onsite

Windshield Replacement (Professional)

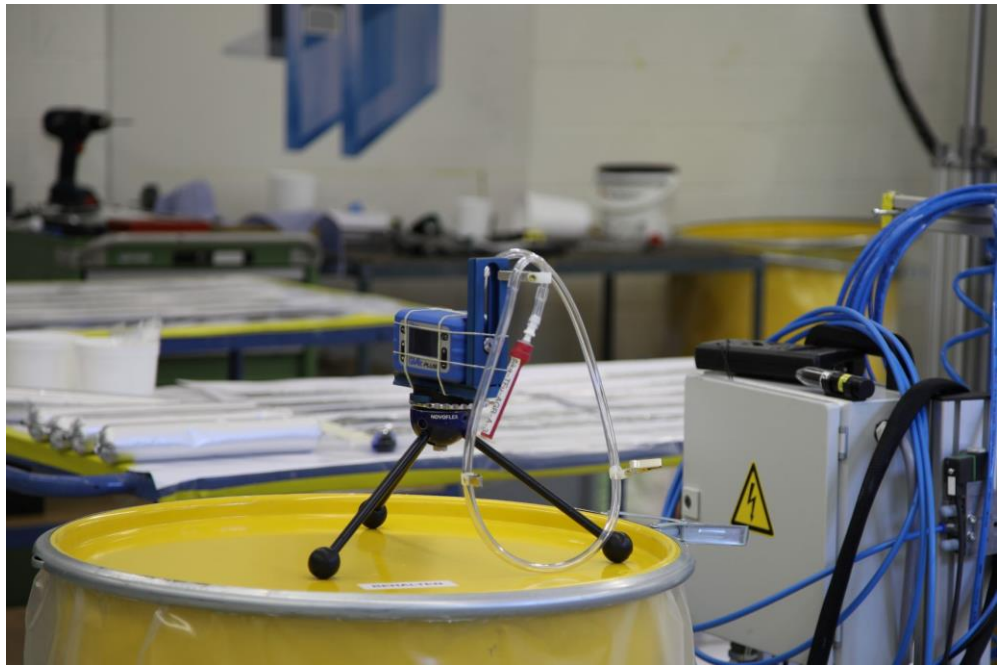
- Direct glazing adhesives are highly viscous and do not form aerosols. The vapour pressure of the polymeric precursors is extremely low. During installation of the windshield, only accidental dermal exposure can be foreseen. Applicators wear protective gloves to prevent dermal contact.
- A typical applicator will have a max. of 10 application jobs, each lasting 40 – 60 min. Most of this time is needed for removing the windshield, preparation and cleaning. The actual working time with the adhesive is < 10 min/job.
- Per application job approx. 350 ml of adhesive are used, the equivalent of approx. 150 – 200 g of polymeric precursor
- The adhesive will cure within several hours

Windshield Replacement (Professional)

- The adhesive container (cartridge or Unipac bag) can be opened without generating any waste
- The cartridge is placed in the application gun and the adhesive is applied from the gun onto the glass. Extruded adhesive is used completely; there is no waste
- After application any adhesive left in the spent cartridge will cure into a solid, cross-linked polymer. The cartridge can then be disposed of as regular waste in compliance with local regulations
- Adhesive waste from trial and similar applications (if any) will also cure into a solid, cross-linked polymer and can be disposed of as regular waste. There is no cleaning of the cartridge, and there will be no discharge of adhesive (polymeric precursor) into the environment

Windshield Replacement (Professional)

Due to the low vapour pressure of polymers, exposure measurements for polymeric precursors are not considered meaningful. Adhesives contain, however, low levels of residual isocyanates which have a somewhat higher volatility. Exposure measurements for such isocyanates under a worst-case scenario (*high number of workplaces per room volume, high number of jobs per shift, no technical room ventilation*) resulted in isocyanate levels below the limit of quantification of the method (< 0.2 ppb).



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Air sampling

Windshield Repair (Professional)

Classification:

- The adhesive carries an H317 phrase (*May cause an allergic skin reaction*) and a H334 phrase (*May cause allergy or asthma symptoms of breathing difficulties if inhaled*)
- Both phrases are driven by residual monomeric isocyanate in the sample; the polymeric precursor does not influence this classification
- Risk management measures are listed on the SDS:
  - P261 Avoid breathing dust/fume/gas/mist/vapours/spray
  - P280 Wear protective gloves/protective clothing/eye protection/face protection/hearing protection/
  - P284 [In case of inadequate ventilation] wear respiratory protection
- The hazard is driven by the monomeric isocyanates of the adhesive. As there is an application step involved, strictly controlled conditions are not possible

Windshield Replacement (Professional)

Application videos

- Shop application of the direct glazing adhesive:

  https://www.youtube.com/watch?v=4yHJM173PUo

  https://www.linkedin.com/posts/beat-zoller-26780815_activity-6887069303254990849-sLLi

- Onsite application of the direct glazing adhesive:

  https://www.youtube.com/watch?v=UnooKolMmjg

‘Reactive PU adhesives’: customized polymeric precursors for dynamic markets

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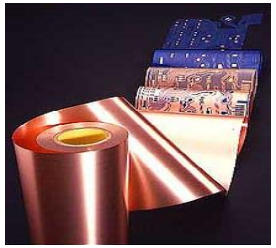
Reactive 100% solvent-free liquid 2-component polyurethanes for lamination of flexible substrates

Industrial lamination of flexible substrates

- **Flexible substrates (plastic films, metal foils, paper) are combined** with a suitable 2-component adhesive to form laminated structures in an industrial process
- Flexible laminates are utilised for flexible packaging (food, pharmaceuticals) and for industrial applications, e.g. printed circuits





- The lamination process discussed in this presentation is based on **polyurethane chemistry**. Details will be shown on the next slide
- The aim of this presentation is to demonstrate that PU laminating adhesives **can be safely handled** under **adequately controlled conditions** without causing harm to humans or the environment

Industrial lamination of flexible substrates

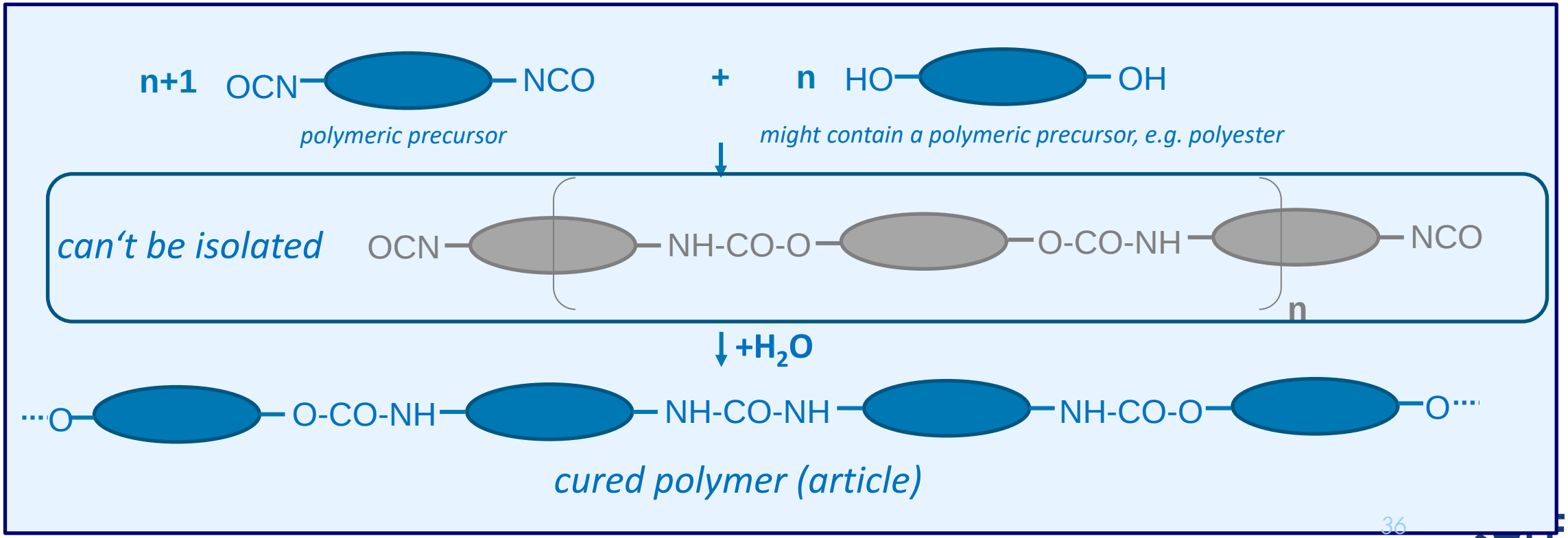
© Henkel

Classification:

- A typical 100% solvent-free adhesive component with reactive isocyanate groups carries
  - H315 (Causes skin irritation)
  - H317 (*May cause an allergic skin reaction*)
  - H319 (Causes serious eye irritation)
  - H334 (May cause allergy or asthma symptoms or breathing difficulties if inhaled)
  - H335 (May cause respiratory irritation)
  - H351 (Suspect of causing cancer)
  - H373 (May cause damage to organs through prolonged or repeated exposure)
- All phrases are driven by residual monomeric isocyanate(s) in the sample; the polymeric precursor does not influence this classification
- Risk management measures are listed in the SDS:
  - P260 Do not breathe mist/spray
  - P280 Wear protective gloves/protective clothing/eye protection/face protection/hearing protection/
  - P284 [In case of inadequate ventilation] wear respiratory protection
- The hazard is driven by the monomeric isocyanates of the adhesive. As there is an application step involved, strictly controlled conditions are not possible.

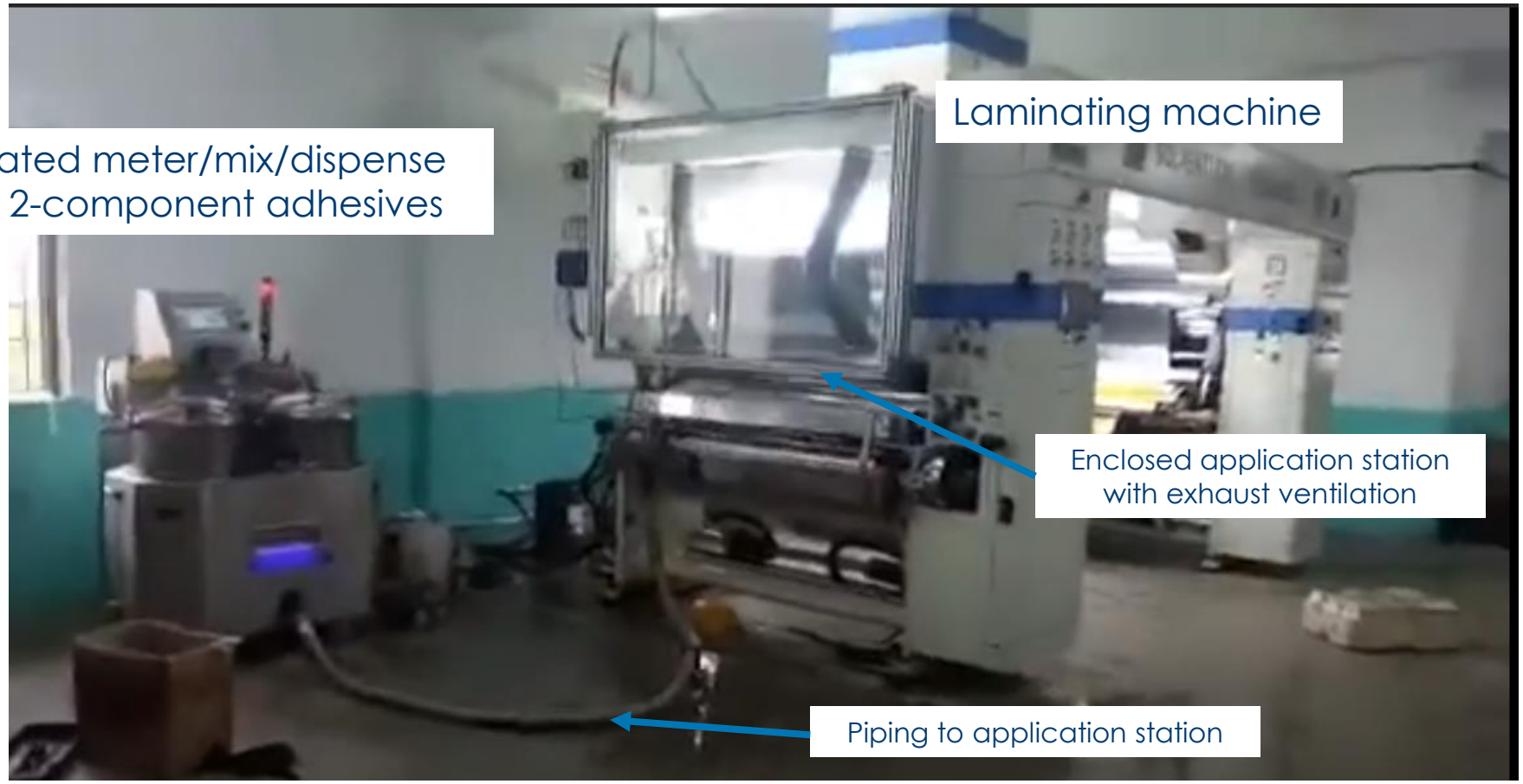
Curing Chemistry

2-component polyurethane chemistry is based on **isocyanate-functional polymers** (*polymeric precursors*) which are mixed prior to use with a hydroxy-functional 2nd component to react to a crosslinked high molecular weight polyurethane with some remaining isocyanate groups. Any excess of Isocyanate groups will react with moisture to a polymer free of any remaining isocyanate group. Both reactions run in parallel and are finalised after a few days at room temperature.



Industrial lamination of flexible substrates

Typical industrial setup



Industrial lamination of flexible substrates

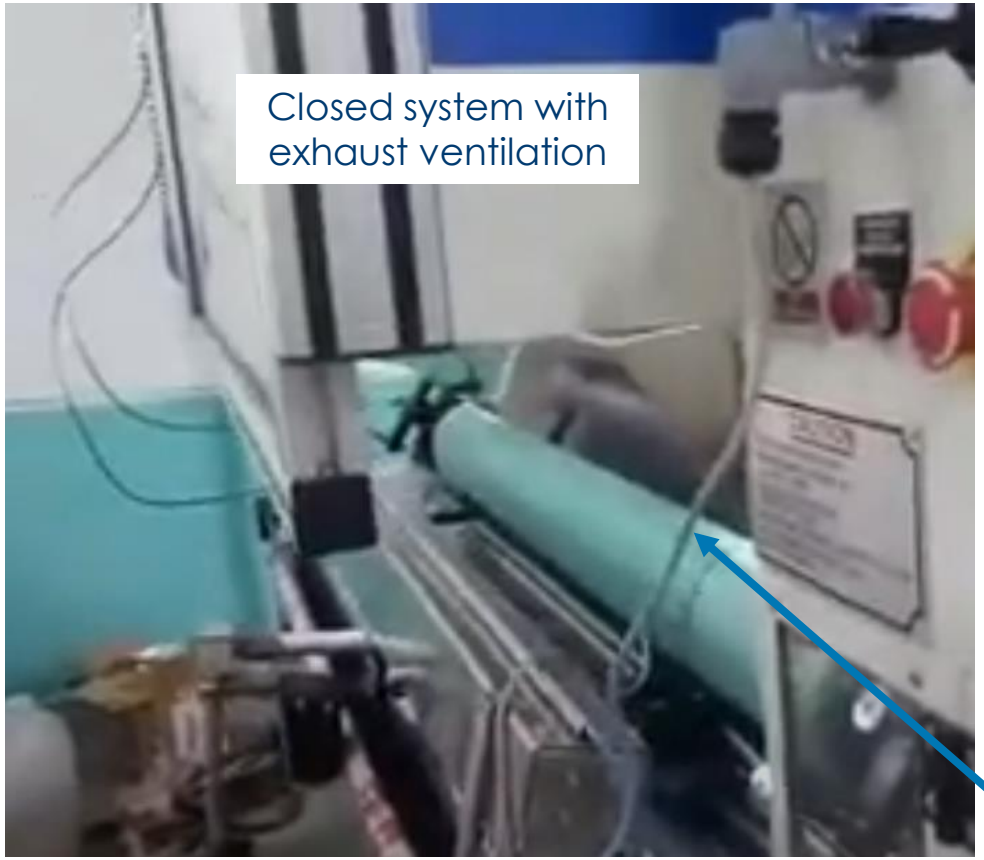
The adhesive is automatically metered, mixed and dispensed directly into the application station of the laminator

Adhesive reservoir tanks for component A & B

Operators wear gloves and respiratory masks for a short period of time to manually refill the reservoir tanks in typically < 15 minutes. During operation, the operators are not exposed to the adhesive.

Industrial lamination of flexible substrates

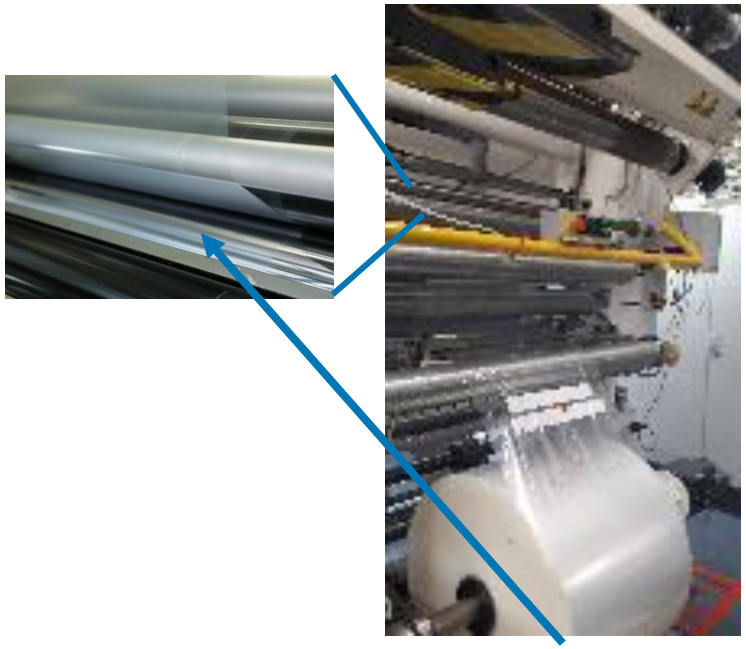
The adhesive is automatically applied with a roller system to the 1st flexible substrate



During operation, the operators are not exposed to the adhesive.
Operators wear gloves and respiratory masks for a short period of time to manually clean the application station in typically < 15 minutes.
Any adhesive waste dripping into a pan below the application station fully cures forming a cross-linked polymer not releasing any component of toxicological concern to human health and the environment.

Industrial lamination of flexible substrates

The laminate is formed by combining the1st flexible substrate carrying the adhesive with a 2nd flexible substrate in a lamination station, with the laminate finally re-winded on a roller



Lamination station

Laminate re-winding on a roll

During the operation, the operators are not exposed to the adhesive. As the adhesive is in between 2 substrates and no adhesive is squeezed out at the edges, operators are not exposed to any adhesive component. Freshly laminated rolls are stored for a few days at room temperature or at 40-45 °C prior to final end-use to ensure that the adhesive has fully cured.

Industrial lamination of flexible substrates

Exposure testing for airborne monomeric diisocyanates

Encapsulated PU adhesive roller application with **exhaust ventilation**

© Henkel

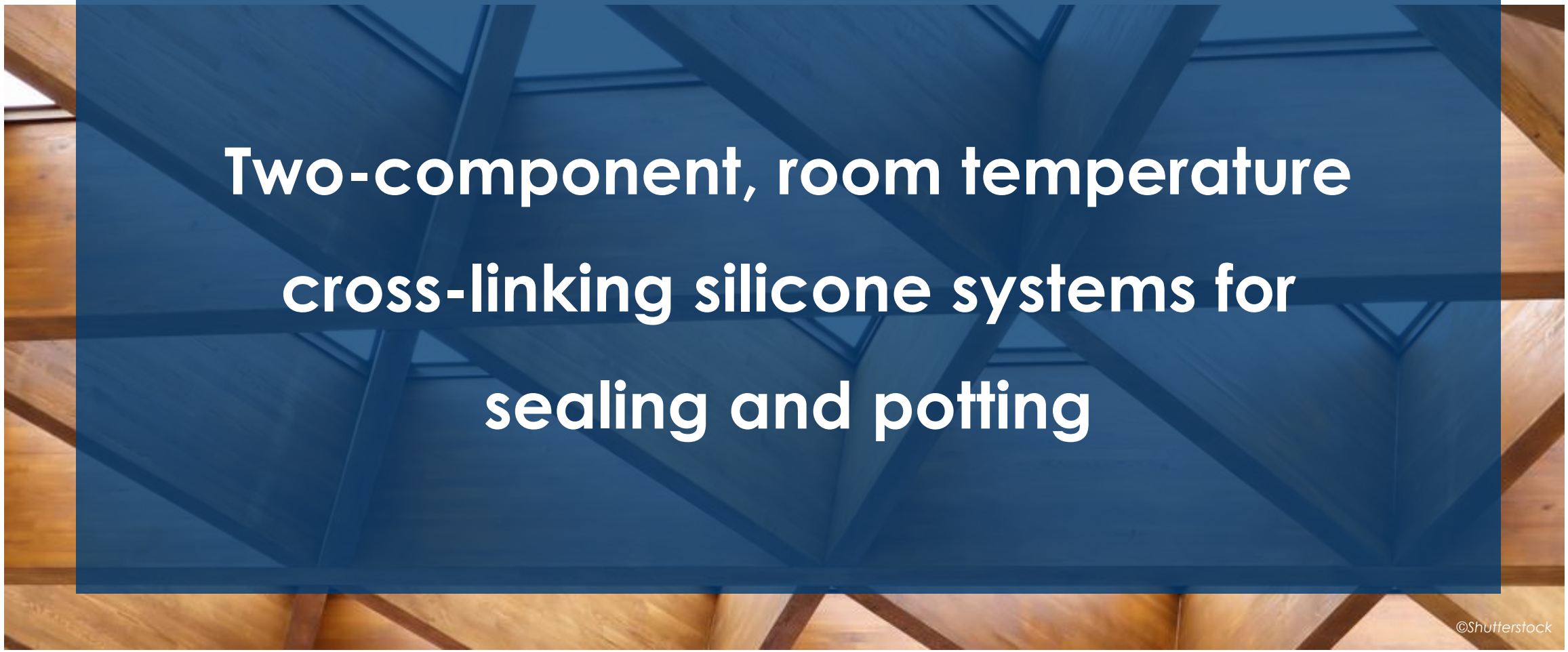
Concentration of airborne monomeric diisocyanates is well below occupational exposure limits at all critical operator positions

Lamination station to combine both films

© Henkel

Implemented risk management measures ensure adequately controlled conditions. Exposure to airborne diisocyanates is regularly tested, being well below occupational safety limits and even detection limits.
The polymeric precursors have a much higher molecular weight than their monomeric diisocyanates and therefore are as well far below occupational exposure limits.
Operators are wearing gloves to exclude any risk of skin contact with monomeric diisocyanates and polymeric precursors.

Two-component, room temperature cross-linking silicone systems for sealing and potting



Introduction

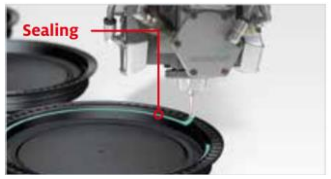
The 2-part silicone develops a cross-linked structure which is extremely resistant to environmental effects such as humidity, dust and temperature and is used, e.g. for:

Electrical engineering
Switch cabinet door

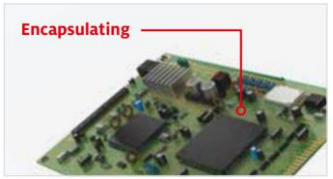
© Henkel

Lighting
Moisture proof luminaire

Packaging covers
suitable for food contact



Electronics
Circuit board protection



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Automotive
Drive belt cover

White goods
Ceramic stovetops

2 component silicone

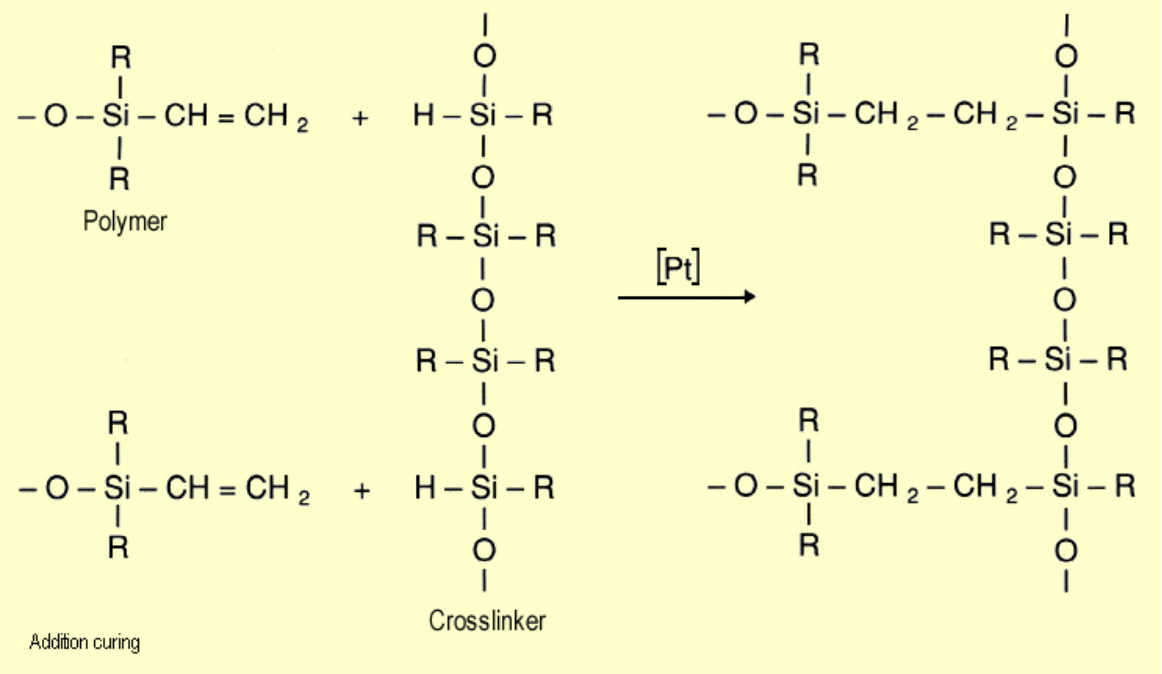
- The two-component silicone system serves for the manufacturing of soft elastic silicone elastomers and silicone foam sealings, which are applied directly onto the part by using Formed In-Place Foam Gasket (FIPFG) technology
- The systems consist of an A-component and a cross-linking B-component, which are mixed with each other in a predetermined mixing ratio
- After mixing the components, most systems react on their own at room temperature and generate a soft elastic silicone foam sealing, or permanently elastic silicone elastomers

A limited number of monomeric and polymeric raw materials are sufficient to develop an infinite number of individual polymer precursors used as reactive silicone systems

Chemistry

Addition curing, by contrast, involves addition of Si-H across double bonds. The catalysts employed here are salts and complexes of platinum (or palladium or rhodium). If platinum-olefin complexes are used, the reaction will occur at room temperature. Platinum-nitrogen complexes require higher reaction temperatures.

Addition curing does not generate any by-products. There is therefore no reduction in weight observed. The reaction is irreversible.



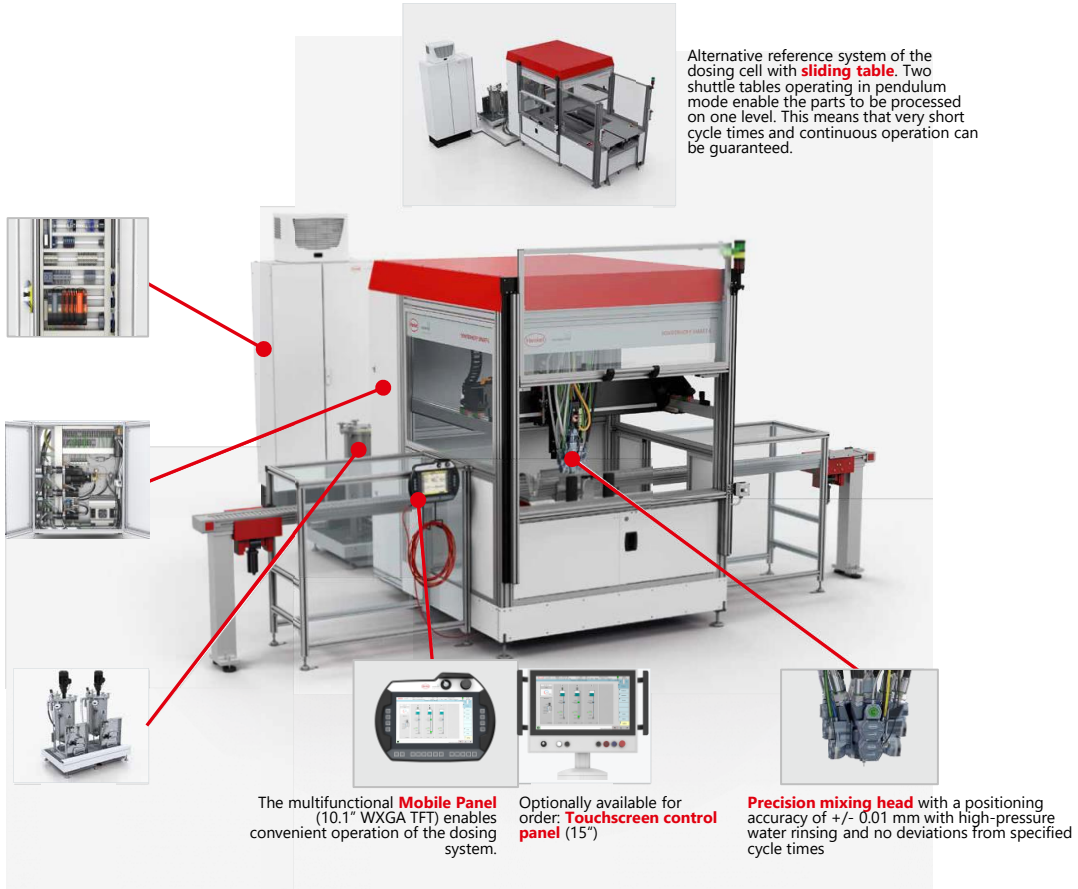
2-component silicone adhesive and sealant

Classification:

- A typical 100% solvent-free silicone adhesive or sealant with reactive Si groups entails
  - H412 (Harmful to aquatic life with long lasting effects)
- All phrases are driven by residual oligomeric siloxane; the polymeric precursor does not influence this classification
- Risk management measures are listed in the SDS:
  - P273 (Avoid release to the environment)
- The hazard is driven by the oligomeric siloxanes of the adhesive or sealant. As there is an application step involved, strictly controlled conditions are not possible

Reference machines & process
Flexible and fully automatic

Customer-specific mixing and dosing systems for accurate and efficient dosing processes



Alternative reference system of the dosing cell with **sliding table**. Two shuttle tables operating in pendulum mode enable the parts to be processed on one level. This means that very short cycle times and continuous operation can be guaranteed.

The electronic control devices, safety engineering and industrial PC are installed in the **control cabinet.**

The **machine cabinet** contains the components of the dosing periphery such as the dosing pumps, the optional Peltier cooling and the high-pressure unit for cleaning the mixing head.

Material pressure tank (24 l or 44 l single-walled or double-walled) with minimum level sensors, on a grating platform with adjustable leveling feet and drip tray

The multifunctional **Mobile Panel** (10.1" WXGA TFT) enables convenient operation of the dosing system.

Optionally available for order: **Touchscreen control panel** (15")

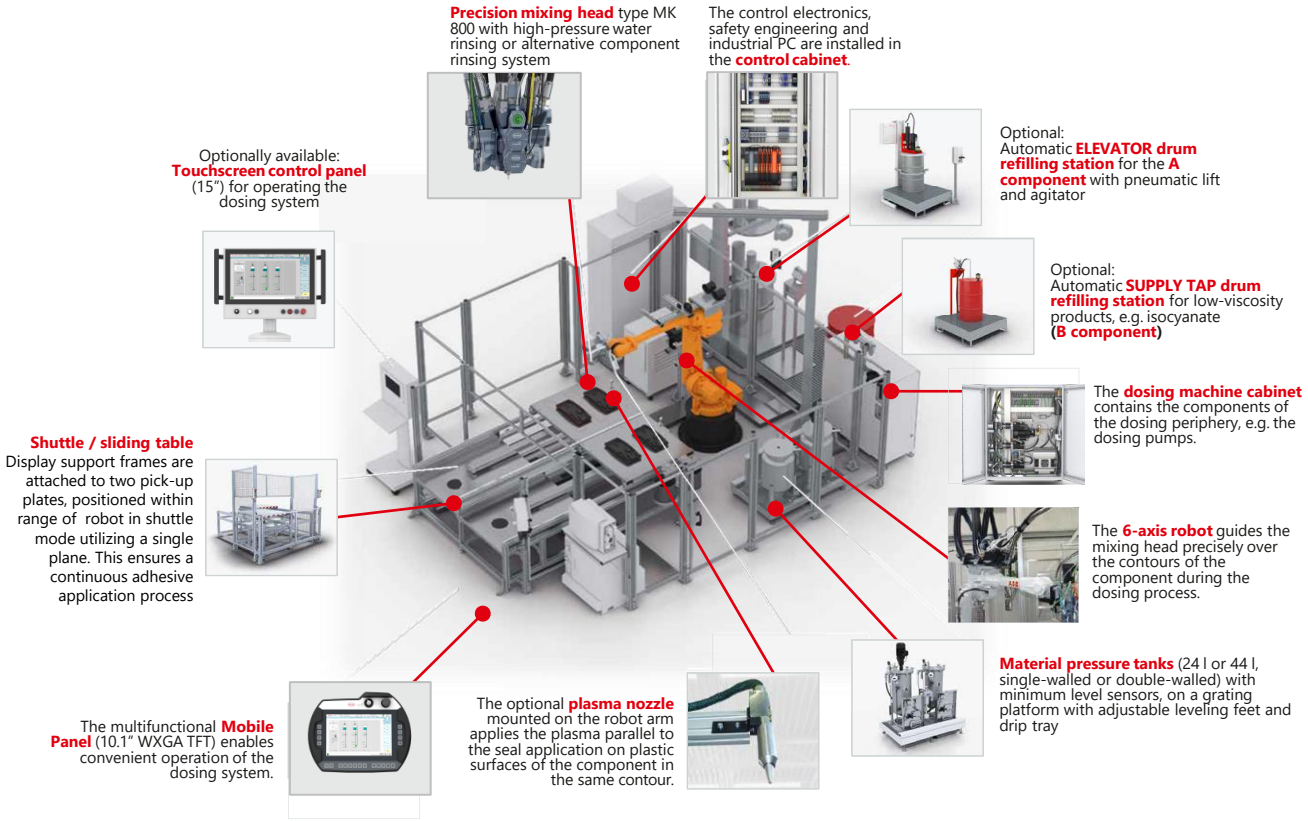
Precision mixing head with a positioning accuracy of +/- 0.01 mm with high-pressure water rinsing and no deviations from specified cycle times

- Equipment for semi- or fully-automatic production systems, using 3- or 6-axis robots
- Ultrasonic sensors are fed for application of sealing foam via conveyor belt system, running through dosing cell
- Despite high volumes of parts and process speeds, dosing cell dispense even smallest quantities into sensor housing
- Minimized maintenance times, consistent dosing quality and traceability of dosing program data during production

Process information on the reference configuration	
Dispensing quantity	1 g/sec.
Dispense time	1.5 sec./part
Component size	20 mm x 10 mm
Cycle time per component	Approx. 3 sec.

Reference machines & process
Flexible and fully automatic

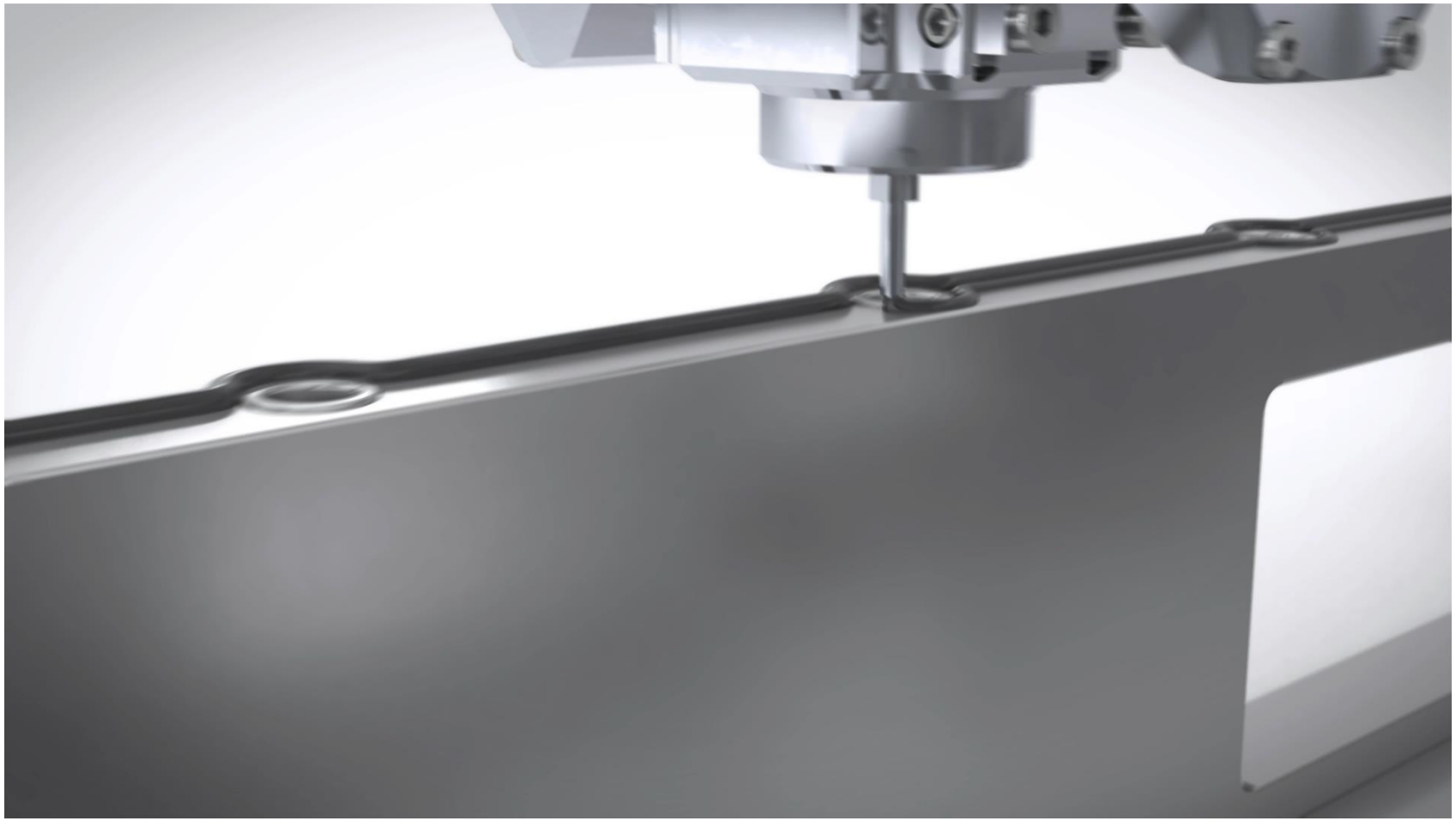
Mixing and dosing system with 6-axis robot guiding mixing head and shuttle table



- Depending on plastic used in support frame, plasma can be applied to contour of display frame beforehand to achieve an improved adhesive effect
- Mixing head mounted on robot arm moves over contour of display frame and applies a precise, narrow bead of adhesive to contour
- Result is a bead of adhesive compensating for height tolerances and remaining consistent after display glass is joined to support frame

Application

PROCESS VIDEO



2-component silicone adhesive and sealant

- Fully automized application process
- Standard personal protective equipment for workers / users (gloves / safety glasses)
- 2-component silicones not containing volatile components even prior to cure
- Exposure to environment main risk (H412)
- Very low concentration of remaining oligomers. Evaluations have shown no release to water/environment
- Sealant between two substrates w/o significant contact with the environment
- Entails cross-linked polymer and disposal as regular waste

Conclusion

Conclusions

- Polymeric precursors are reactive polymers with some still containing their reactive monomeric building blocks. They cure after application in a short period of time (hours to days) to high molecular weight polymers and are no longer present after curing
- In the particular case of adhesives being applied to bond two substrates together, such polymeric precursors react immediately after application and do not carry any risk of exposure
- Adequately controlled conditions based on the classification of the components are already implemented today and defined by the classification of the monomers or other components as part of the mixture with the polymeric precursor
- At all stages of the industrial manufacturing of polymeric precursors as well as at application by downstream users, Occupational Safety & Health standards apply. In the particular case of polyurethane polymeric precursors, regular mandatory training required by the new Reach restriction on diisocyanates will further improve the protection of human health and the environment

MORE INFORMATION

Interested in FEICA positions on the upcoming registration of polymers?

https://www.feica.eu/our-priorities/reach/polymers-requiring-registration

CONTACT FEICA

info@feica.eu

www.feica.eu