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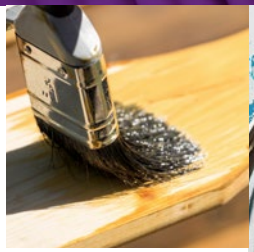
High Performance Polyurethanes



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Polyurethanes 06

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By U. Meier-Westhues, K. Danielmeier, P. Kruppa, E. P. Squiller

BOOK EXCERPT: Polyurethanes

DEEP INSIGHT | EMULSION BINDERS

A sustainable alternative for wood coatings 52

Self-crosslinking polyacrylate emulsion with 35 % biomass content.
By Remko de Zwart, Craig Frankum, Daan Huisman and Esther Grau Zuriaga | ***Covestro***

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PLUS

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DEEP INSIGHT | PRODUCT OVERVIEW

A perfect fit 65

This overview shows different polyurethane dispersions for the use in coating systems.
By Katrin Vogt

DEEP INSIGHT | ADDITIVES

Lasting Release 67

New silicone additives for high-performance anti-graffiti polyurethane applications.
By Dmitry Chernyshov | ***Momentive Performance Materials***

DEEP INSIGHT | CROSSLINKERS

Cyclic carbonate, not isocyanate 73

Glycerol sourced from biodiesel may provide an alternative to isocyanate polyurethanes in coating applications.
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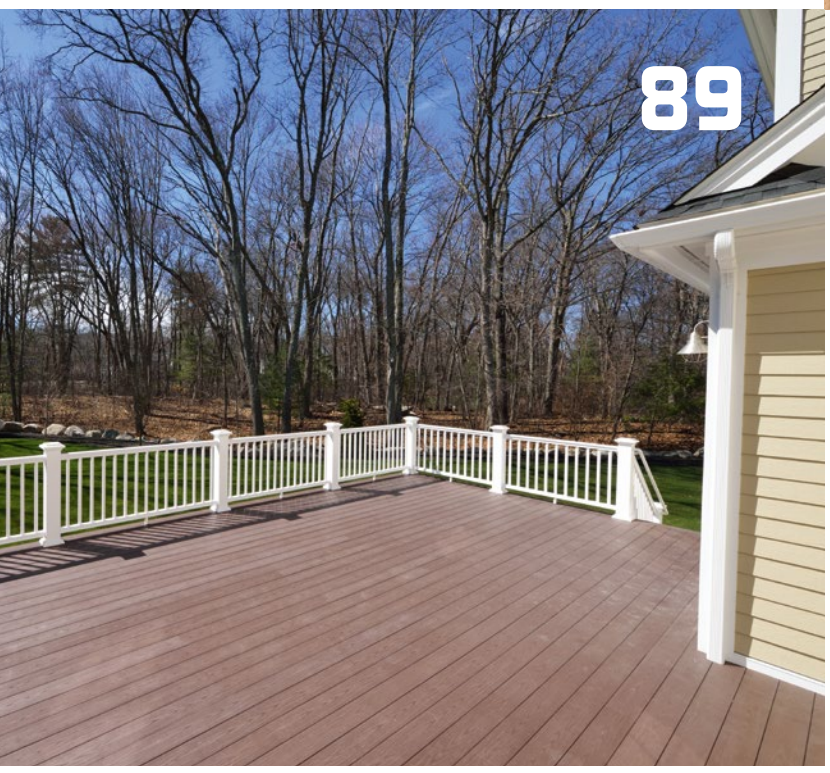

DEEP INSIGHT | LIFE CYCLE

Towards a smaller footprint 95

Contributing to the development of more sustainable solutions for wood coatings.
By Dr Eva Tejada and Daniel Steinke | ***Covestro***

PLUS

- **VIDEO: A corrosion diary by EIS: Life span of solvent-free polyurethanes. By Merve Demirkurt, Kanat Paint**
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DEEP INSIGHT | APPLICATION

Doubly Greens 102

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By Michael Shen | ***DuPont Tate & Lyle Bio,***
Tianxiang Chen and Guiyou Wang | ***East China University of Science and Technology***

DEEP INSIGHT | APPLICATION

From analogue to digital 107

Advances in the digital application of polyurethane-based coatings and adhesives..
By Dr Inga Bargende, Dr Ann-Christin Bijlard-Jung, Dr Fabian Schuster | ***Covestro***

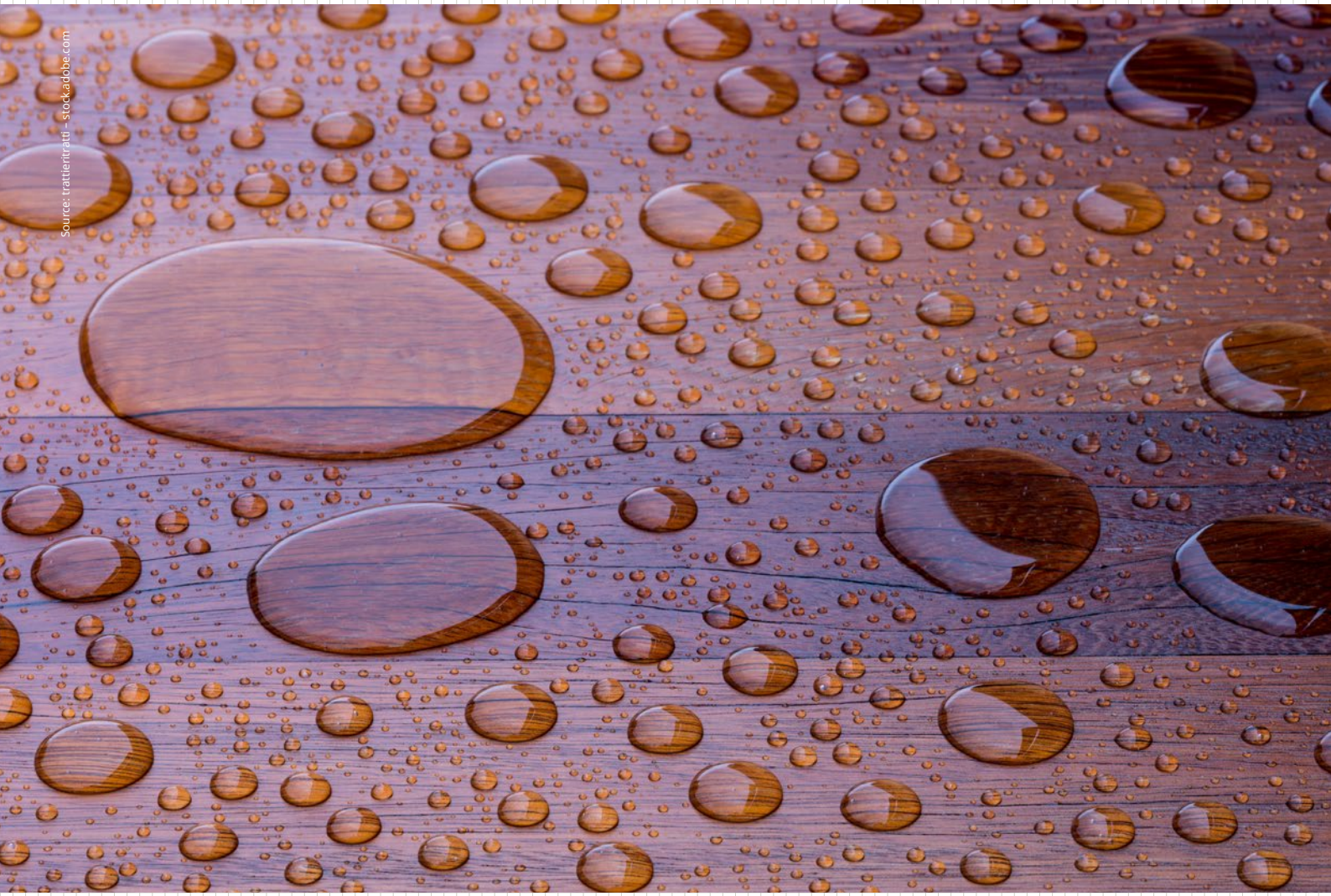
DEEP INSIGHT | MARKET REPORT

An inherently sustainable sector 113

The global protective coatings market will maintain strong growth.
By Sarah Silva

POLYURETHANES

In this article you will learn the basic chemistry of polyurethanes and how they react with polyols, polyamines, polyacrylates and hybrids via mono-, di- and poly-isocyanates and blocked isocyanates to form polyurethanes. Emphasis is placed on the aspect of aqueous polyurethane formulations.



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3 Chemical principles

3.1 Diisocyanates

Polyurethanes are obtained by the reaction of polyfunctional polyols (in coatings formulations often referred to as component A) and polyfunctional isocyanates (component B). The latter are synthesized by oligomerization of monomeric diisocyanates. The diisocyanates are usually prepared on an industrial scale by liquid or gas phase phosgenation of their corresponding primary amines, and subsequent removal of the excess of monomeric isocyanates (see Figures 3.1 and 3.2).[1, 2]

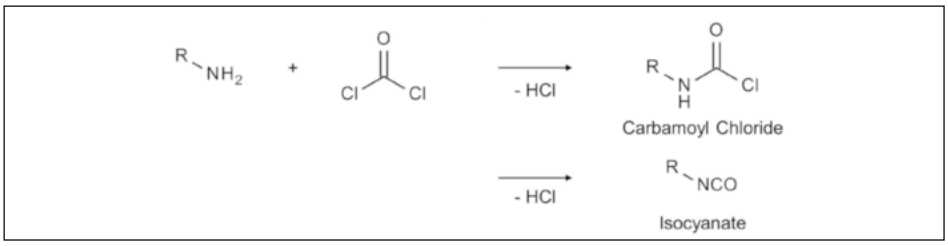


Figure 3.1: Manufacture of isocyanates by phosgenation of primary amines

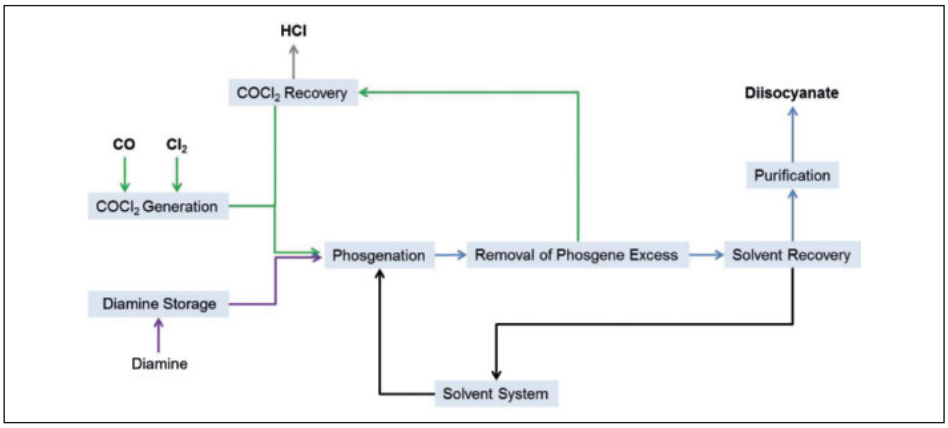
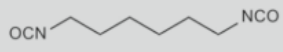
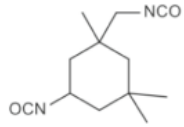
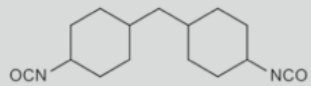
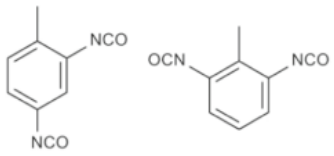
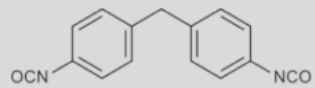
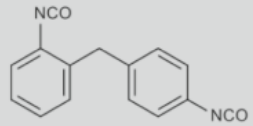


Figure 3.2: Principal technical procedure of manufacture of diisocyanates by phosgenation

Chemical principles

Table 3.1: Industrial diisocyanates

	Manufacturers/trade names
Hexamethylene diisocyanate (HDI) 	Covestro: "Desmodur" H BASF: "Basonat" H" Vencorex: "Tolonate" Wanhua: "Wannate" HDI Asahi KASEI: "Duranate" 50M-HDI
Isophorone diisocyanate (IPDI) (3-Isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate) 	Covestro: "Desmodur" I Evonik: "Vestanat" IPDI Wanhua: "Wannate" IPDI
Bis-(4-isocyanatocyclohexyl)methane (H_{12}MDI) 	Covestro: "Desmodur" W Evonik: "Vestanat" H_{12}MDI Wanhua: "Wannate" HMDI
2,4- and 2,6-Toluene diisocyanate (TDI) 	Covestro: "Desmodur" T BASF: "Lupranat" T Dow Chemical: "Voranate" T Vencorex: "Scuranate" T
Diphenylmethane 4,4'- and/or  -2,4'-diisocyanate (MDI) 	Covestro: "Desmodur" 44 M BASF: "Lupranat" M Dow Chemical: "Isonate" Huntsman: "Suprasec" Wanhua: "Wannate" MDI and/or Covestro: "Desmodur" LS 2424

Alternatively, for selected aliphatic diisocyanates, phosgene-free manufacturing processes have been developed. One such process involves the reaction of an amine and an alcohol with a urea to give a urethane that is then split at elevated temperatures to yield an isocyanate. This process is also used in the industrial production of some diisocyanates, such as bis-(4-isocyanatocyclohexyl) methane (see Figure 3.3).[3]

The standard commercial polyisocyanates used in coatings and adhesives are all derived from just a few diisocyanates with aliphatically, cycloaliphatically or aromatically

bound isocyanate groups.[4] The most important diisocyanates that are available on an industrial scale are summarized in Table 3.1.

In addition to these, a number of other monomeric diisocyanates for the manufacture of specialty coating and adhesive raw materials have been described. However, these have yet to achieve widespread industrial significance. Pentamethylene diisocyanate (PDI) is the most recent example.[4] This product, in contrast to petrochemical based diisocyanates, is produced from a renewable feedstock with improved carbon footprint versus hexamethylene diisocyanate (HDI). Table 3.2 shows some examples of diisocyanate specialities.

With the exception of MDI which has accorded special status on account of its low vapor pressure, other monomeric diisocyanates have a significant volatility. For occupational health reasons, monomeric diisocyanates are generally not used as coating and adhesives raw materials. To overcome the hazardous potential related to diisocyanate monomers and to achieve low volatility, they must first be converted into higher molecular weight polyisocyanates, using suitable modification reactions like the formation of water-borne polyurethane dispersions, UV curable resins, prepolymers, and polyisocyanate crosslinkers. When necessary, the removal of the monomeric diisocyanates is done as part of the production process of these modified products. These components and different classes of polyurethane resins will be covered in subsequent chapters.

3.2 Isocyanate reactions

The most important type of reactions involving isocyanates is the addition of compounds containing active hydrogen atoms, especially polyols, polyamines, and to some much lesser extent thiols and carboxylic acids. Table 3.3 provides an overview of basic reactions of the isocyanate group.

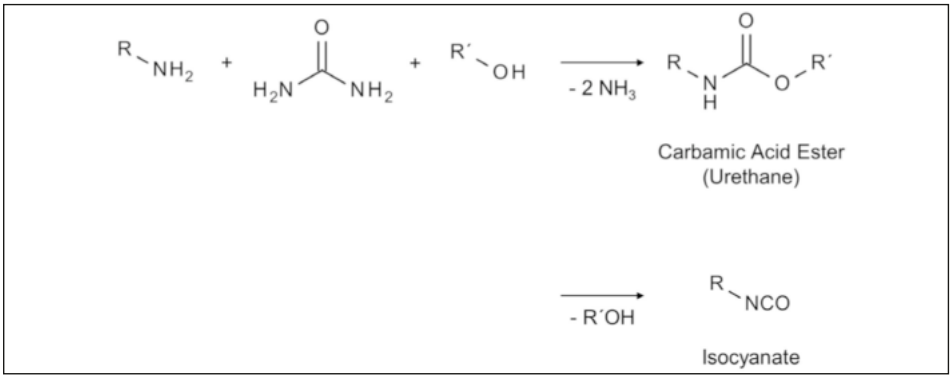
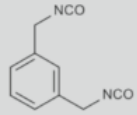
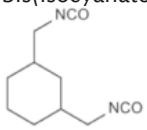
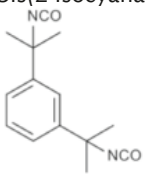
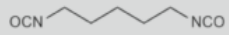
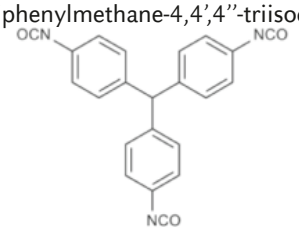
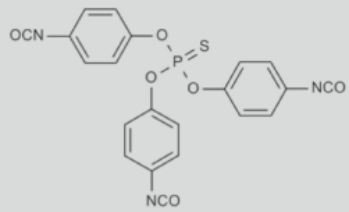


Figure 3.3: Manufacture of organic isocyanates via the urea route

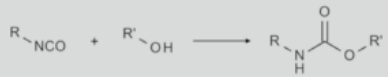
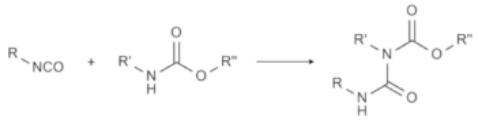
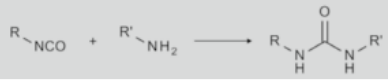
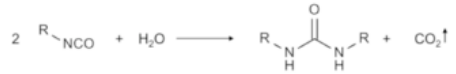
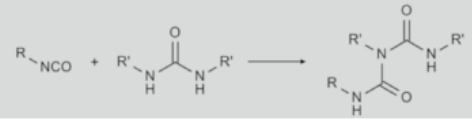
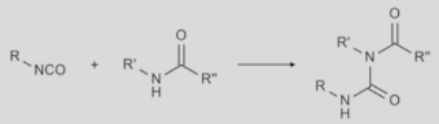
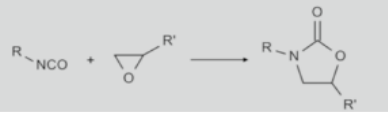
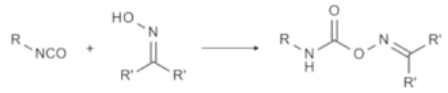
Polyurethane coatings

Table 3.2: Diisocyanate specialties (selection)

	Manufacturer/trade name
Xylylene diisocyanate (XDI) 1,3-bis(isocyanatomethyl)benzene 	Mitsui Chemicals: “Takenate” 500
Hydrogenated xylylene diisocyanate (H_6-XDI) 1,3-bis(isocyanatomethyl)cyclohexane 	Mitsui Chemicals: “Takenate” 600
2,2,4- and 2,4,4-Trimethyl-1,6-diisocyanatohexane 	Evonik: “Vestanat” TMDI
Tetramethylxylylene diisocyanate (TMXDI)[5] 1,3-bis(2-isocyanatoprop-2-yl)benzene 	Allnex: TMXDI
1,5-Pentamethylene diisocyanate 	Covestro: “Desmodur” P Mitsui Chemicals: “STABiO”
Triphenylmethane-4,4’,4’’-triisocyanate 	Covestro: “Desmodur” RE
Tris(p-isocyanatophenyl)thiophosphate 	Covestro: “Desmodur” RFE

Isocyanate reactions

Table 3.3: Schematic reaction principles of isocyanates

Reaction with	Reaction equation
Alcohol to urethane	
Urethane to allophanate	
Amine to urea	
Water to urea	
Urea to biuret[7]	
Carboxylic acid to amide[8a]	
Amide to acyl urea	
Anhydride to imide	
Epoxide to oxazolidone	
Oxime to oxime carbamate	
Carbon dioxide to oxadiazinetrione[8b]