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Introduction

During the late 1930’s, Otto Bayer and his co-workers pioneered the chemistry of polyisocyanates, a technology which led to the advent of polyurethanes for a variety of applications.

Since 1955 Bayer Corporation has introduced a variety of monomeric and polymeric isocyanates, polyesters, polyethers, and acrylics for use in the formulation of polyurethane coatings. Unlike alkyd or melamine-cured systems, polyurethane coatings are based upon a well-defined stoichiometry. This feature allows the design of polyurethane coating systems to meet specific end-use requirements.

This brochure is intended to provide the coatings formulator with background information on the chemistry of one- and two-component polyurethane coating systems. Further information from Bayer Corporation in the form of Product Information Bulletins and applications literature is available from your Bayer MaterialScience representative or distributor.

General Information

The isocyanate group can react with any compound containing a reactive hydrogen. The three reactions shown in Figure 1 are of principal interest. Reaction of an isocyanate with an alcohol yields a urethane; reaction of an isocyanate with an amine yields a urea, and reaction of an isocyanate with water results in intermediates which decompose to yield carbon dioxide and an amine; which further reacts to again form a urea. Other potential isocyanate coreactants include carboxylic acids, urethanes and ureas.

In order to prepare polymeric materials, the reaction partners must have at least two functional groups per molecule (Figure 2). Linear polymers are formed when both reaction partners are difunctional. Three-dimensional networks require that at least one of the reaction partners has three or more reactive groups.
The isocyanate group can also undergo self-condensation. For example, three isocyanates can be trimerized to form the isocyanurate ring as shown in Figure 3.

**Figure 3 Formulation of the isocyanurate ring**

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**Nomenclature**

The trade names for the products discussed in this brochure are as follows:

- **Desmodur and Mondur**
  - Aliphatic and aromatic diisocyanate monomers and polyisocyanates.

- **Desmophen**
  - Hydroxyl-functional polyester, polyether, and acrylic reaction partners for Desmodur and Mondur polyisocyanates.

- **Desmophen NH**
  - Amine functional, polyaspartic acid ester reaction partners for Desmodur and Mondur polyisocyanates.

- **Rucote**
  - Hydroxyl-functional polyester resins for thermoset polyurethane powder coatings.

- **Acclaim, Arcol and Multranol**
  - Hydroxyl-functional polyether polyols.

- **Desmolith**
  - Polyalcohol emulsion coreactant for Desmodur and Mondur polyisocyanates.

- **Desmolux**
  - Acrylate functionalized resins for UV and EB cured coatings.

- **Desmodur BL and Desmotherm**
  - Blocked polyisocyanates for baking finishes.

- **Desmocap**
  - Aromatic blocked polyisocyanates for room temperature cure and flexibilizing epoxies.

- **Crelan**
  - Crosslinkers for thermoset polyurethane powder coatings.

- **Desmolac**
  - High molecular weight polyurethane lacquer resins.

- **Impranil**
  - Polyurethane resin solutions and aqueous dispersions for textile coatings.

- **Bayhydrol and Baybond**
  - Aqueous polyurethane dispersions and hydroxyl functional polyurethane dispersions, acrylics and polyesters.

- **Bayhydur**
  - Aliphatic polyisocyanates for water-based systems.

- **Bayhydrol UV**
  - Urethane acrylate dispersions for UV and EB cured coatings.

Many of Bayer’s polyisocyanate coatings products employ a system which, in most cases, stipulates the product family, monomeric diisocyanate starting material, and weight solids. Familiarity with the nomenclature will allow a quick determination of the chemical basis for most of Bayer’s coatings products, and can best be understood by looking at the example in Table 1.
As with any system, notable exceptions exist, especially in the Desmodur N and Desmodur L polyisocyanate families (Table 2). These products were established long before an attempt was made to switch to a more uniform system of nomenclature. Also, experimental product designations may not fit into the commercial nomenclature system.

Table 1
Nomenclature

<table>
<thead>
<tr>
<th>Monomer Designation</th>
<th>Product Family**</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 = Toluene Diisocyanate—TDI</td>
<td>BL = Blocked</td>
</tr>
<tr>
<td>2 = Diphenylmethane—E = Moisture Cure</td>
<td></td>
</tr>
<tr>
<td>3 = Hexamethylene Diisocyanate</td>
<td>N = Hexamethylene Diisocyanate Based</td>
</tr>
<tr>
<td>4 = Isophorone Diisocyanate—IPDI</td>
<td>Z = Isophorone Diisocyanate Based</td>
</tr>
<tr>
<td>5 = Bis(4-Isocyanatocyclohexyl) Methane—H12MDI</td>
<td>L = Toluene Diisocyanate based</td>
</tr>
</tbody>
</table>

Table 2
Nomenclature exceptions

Polyisocyanates based on HDI:
- Desmodur N-75
- Desmodur N-100
- Desmodur N-751

Polyisocyanates based on TDI:
- Desmodur L-75
- Desmodur L-67 MPA/X
- Desmodur L67 BA

Monomeric Diisocyanates

Monomeric diisocyanates are major building blocks for the value-added polyurethane products most commonly used in the coatings industry. There are important differences between aromatic and aliphatic diisocyanate monomers. Aromatic diisocyanates are much more reactive than their aliphatic diisocyanate counterparts. Urethane products made from aromatic diisocyanate monomers oxidize more easily than those prepared from aliphatic diisocyanates, especially when exposed to UV light. The higher resistance to UV light-induced degradation of products prepared from aliphatic diisocyanates make them more useful in high quality exterior coatings where gloss and color retention are most important.
Toluene Diisocyanate (TDI)

One of the most important monomers used in the polyurethane industry is toluene diisocyanate. In the coatings industry it is mainly used as a raw material in preparing adducts and prepolymers. TDI is also used as a modifier in alkyd resins. The two commercial isomers of TDI are shown in Figure 4. Bayer markets three versions of TDI under the following trademarks:

- Mondur TD — 65/35 mixture of 2, 4 and 2, 6 isomers
- Mondur TD-80 — 80/20 mixture of 2, 4 and 2, 6 isomers
- Mondur TDS — 2, 4 isomer

Mondur TD-80 is supplied in two different grades varying in acidity.

Diphenylmethane 4, 4’ - Diisocyanate (MDI)

One of the first diisocyanate monomers to achieve widespread industrial use was diphenylmethane 4, 4’ - diisocyanate, shown in Figure 5. Bayer markets MDI under the trademark Mondur M and supplies the material as a fused solid, a flaked solid, or a liquid.

Diphenylmethane 2, 4’ - Diisocyanate

Bayer also supplies an isomer mixture of MDI containing 55% 2,4’ isomer shown in Figure 5, and 45% of the 4, 4’ isomer shown in Figure 4 under the trademark Mondur ML. The isomer mixture allows this product to maintain a liquid supply form.
Hexamethylene Diisocyanate (HDI)

Another important diisocyanate monomer used for the preparation of a wide variety of polyisocyanate adducts used in exterior polyurethane coatings is hexamethylene diisocyanate, shown in Figure 7. This material is marketed by Bayer under the trademark Desmodur H.

Bis(4-isocyanatocyclohexyl) Methane

The monomeric diisocyanate shown in Figure 8, bis(4-isocyanatocyclohexyl) methane, is sold by Bayer under the trademark Desmodur W.

Desmodur W is also known as hydrogenated MDI (HMDI or H12MDI), reduced MDI (RMDI), or saturated MDI (SMDI). It is a useful material for the production of hydrolytically stable polyurethanes and dispersions, as well as prepolymers for weatherable one- and two-component formulations, cast elastomers, and for powder coating crosslinkers.

Isophorone Diisocyanate (IPDI)

Marketed under the Desmodur I trademark, isophorone diisocyanate is a useful building block in the production of light-stable polyurethanes. Typical resin types manufactured with IPDI include polyurethane dispersions and lacquers, prepolymers for one- and two-component formulations, radiation curable oligomers, and powder coating crosslinkers. The structure of IPDI is shown in Figure 9.

Polyisocyanates

Industrial hygiene concerns limit the use of monomeric diisocyanates directly in most typical coatings applications. Higher molecular weight resins such as adducts, prepolymers, and isocyanurate trimers are preferred because they contain only very low levels of monomeric diisocyanate. A low level of monomeric diisocyanate reduces the concerns associated with manufacturing and handling polyurethane coatings.
TDI Based Polyisocyanates

Two different types of aromatic polyisocyanates manufactured from TDI are available. Desmodur L polyisocyanate is a TDI-trimethylolpropane (TMP) adduct that is available in several solvent blends. Desmodur IL polyisocyanate is the isocyanurate trimer of TDI. Idealized structures are shown in Figures 10 and 11.

Both Desmodur L and Desmodur IL polyisocyanates are used in two-component industrial coatings. Desmodur IL is particularly useful in applications where extremely rapid curing is desired. Desmodur L and Desmodur IL should not be used where exterior lightfastness and gloss retention are required.

MDI Based Polyisocyanates

In addition to the two forms of Mondur M (monomeric 4,4’ MDI) and Mondur ML (MDI isomer blend) diisocyanates discussed before, oligomeric mixtures of the type shown in Figure 12 are marketed under the trademarks Mondur MR, Mondur MRS, Mondur MRS 4, Mondur MRS 5 and Desmodur VL. These materials, commonly referred to as “polymeric MDI,” are supplied as low viscosity liquids containing no solvent, and are used to prepare high-solids or solvent-free coatings, caulks, sealants and adhesives.

The Mondur MR products are characterized by a lower 2, 4’ isomer content and higher functionality. The higher 2, 4’ isomer content of the Mondur MRS products can result in slower rates of reaction, form lower viscosity prepolymers, and demonstrate improved compatibility with some polyether polyols. Desmodur VL polyisocyanate gives a balance of potlife and reactivity that makes it the polyisocyanate of choice in some coatings and the polymer concrete formulations containing Desmolith polyols.
Either one- or two-component coatings can be prepared from these polyisocyanates. These polyisocyanates also should not be used where exterior lightfastness and gloss retention are important.

**Figure 12**

MDI oligomers

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**HDI Based Polyisocyanates**

Polyisocyanates based on HDI represent the most important class of polyisocyanates used today in polyurethane coatings. Coatings prepared with these products can have excellent resistance to chemicals and abrasion and superior weathering characteristics, including gloss retention and resistance to yellowing and chalking.

One commercial class of HDI polyisocyanates includes Bayer’s Desmodur N-75, Desmodur N-100, and Desmodur N-3200, which are polymeric materials containing biuret groups (Figure 13). Desmodur N-75 polyisocyanate, available in a number of solvent supply forms, is a 75% solids version of Desmodur N-100 polyisocyanate. Desmodur N-3200 polyisocyanate is a low viscosity version of Desmodur N-100 polyisocyanate.

**Figure 13**

The biuret of HDI

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Like TDI, HDI can be converted to a trimer that contains an isocyanurate ring (Figure 14). These products are marketed under the trademark Desmodur N-3300, and the 90% solids version, Desmodur N-3390. Desmodur N-3600 polyisocyanate is a low viscosity version of the Desmodur N-3300 polyisocyanate. Desmodur N-3790 polyisocyanate is a higher functionality, fast drying polyisocyanate developed for automotive refinish and industrial coatings. Desmodur N-3800 polyisocyanate is a flexibilized trimer developed for coatings of plastics, soft feel coatings, stone-chip protection systems and as a blending resin modifier. Trimers of HDI are characterized by lower free monomer content than the biurets, and in some cases, improved exterior weatherability.

**Figure 14**

The isocyanurate ring of HDI
The asymmetric trimers are the newest family of polyisocyanates based on HDI developed to meet the demand for high performance, higher solids coatings. The asymmetric ring structure (Figure 15) yields polyisocyanates characterized by low-free monomer content and excellent exterior durability combined with low resin viscosity. The ability to achieve low viscosity while maintaining functionality leads to a better property balance in the coating formulation. The asymmetric trimer of HDI is currently marketed under the trademark Desmodur XP 2410.

Desmodur N-3400 polyisocyanate is a blend of the trimer (Figure 14) and uretdione (Figure 16) of HDI. Characterized by a very low viscosity compared to other HDI polyisocyanates, Desmodur N-3400 is usually used in blends with the other HDI polyisocyanates in formulating higher solids polyurethane coatings. Desmodur N-3400 is not generally used as the sole polyisocyanate in an exterior polyurethane formulation because of lower functionality.

An isocyanurate copolymer of TDI and HDI (Figure 17) is marketed under the trademark Desmodur HL. As expected, the properties of films prepared from Desmodur HL polyisocyanate are intermediate between those prepared from the individual trimers, Desmodur IL and Desmodur N-3300 polyisocyanates.

**IPDI Based Polyisocyanates**

Isocyanurate trimers based on IPDI are marketed by Bayer under the trademark Desmodur Z-4470 (Figure 18). Available in a number of solvent blends, these polyisocyanates are less reactive than Desmodur N polyisocyanates and produce more rigid films. Two-component polyurethanes formulated with Desmodur Z-4470 as the sole polyisocyanate or in blends with Desmodur N polyisocyanates generally have shorter tack free times than when using Desmodur N types as the sole polyisocyanate. Desmodur Z polyisocyanates are compatible with alkyd paints containing aliphatic hydrocarbon solvent blends. Addition of Desmodur Z polyisocyanates to these paints usually results in faster drying properties, harder films, and improved gloss.
Blocked Polyisocyanates

The polyisocyanates described thus far contain ready to react isocyanate groups. In typical two-component formulations, these polyisocyanates are usually combined with the polyol component just prior to application. When the polyisocyanate and the polyol are mixed, they immediately begin to react with one another, which leads to a limited, although usually adequate, potlife.

Another group of Desmodur products contains isocyanate groups that are blocked by compounds such as ε-caprolactam, butanone oxime, phenol, or dimethylpyrazole. At room temperature, these blocked polyisocyanates do not react with polyols at any appreciable rate. At elevated temperatures the blocked polyisocyanate liberates the blocking agent, which may leave the film (Figure 19), and the polyisocyanate reacts with the polyol. This means that one-component, room-temperature stable coatings can be formulated with blocked polyisocyanates and suitable polyol components. The use of blocked polyisocyanates also allows the formulation of stable water-based one-component polyurethane formulations. Crosslinked polyurethane films can be prepared at temperatures as low as 230°F with properties similar to those of corresponding two-component systems.

In addition there are new product developments based on blocking agents such as diethyl malonate which do not react according to the mechanism depicted in Figure 19.

The type of blocking agent as well as the addition of catalysts can strongly influence the baking temperature required to develop the desired coating properties. Figure 20 demonstrates these effects with one base polyisocyanate and polyol combination.
For the formulation of one component polyurethane coatings, Bayer markets a wide range (in base polyisocyanate and blocking agents) of blocked aliphatic polyisocyanates under the trademarks Desmodur BL and Desmodur PL.

A special group of blocked polyisocyanate products are marketed under the Desmocap trademark. These products have been developed to crosslink at room temperature with aliphatic amines. The blocking agent, in this case, will stay in the coating film. They are especially useful as flexibilizing agents for 100% solids cycloaliphatic amine-cured liquid epoxy systems.

Bayer supplies a variety of blocked isocyanates for liquid coatings under the following trademarks:

- Desmodur PL-350 — Dimethylpyrazole blocked HDI isocyanate
- Desmodur BL-3175A — Butanone oxime blocked HDI isocyanate
- Desmodur BL-4265 — Butanone oxime blocked IPDI isocyanate
- Bayhydur VP LS 2310 — Water dispersed butanone oxime blocked HDI isocyanurate
- Bayhydur VP BL 5140 — Water dispersible butanone oxime blocked Desmodur W polyisocyanate
- Desmocap 11A — Substituted phenol blocked TDI prepolymer
- Desmocap 12A — Substituted phenol blocked TDI prepolymer

Blocked isocyanates is an area of active development. Contact Bayer for the full range of latest developments.

**Powder Coatings**

In addition, solid blocked polyisocyanates are available which can be used in the formulation of storage stable thermoset powder coatings. These solid supply form blocked polyisocyanate hardeners or curing agents are primarily used with solid, hydroxyl-functional polyesters or polyacrylates in the formulation of polyurethane powder coatings. They are also used for supplemental crosslinking in epoxy/polyester hybrid and TGIC/polyester thermoset powder coatings. Bayer markets polyisocyanate powder curing agents under the Crelan trademark.

**Crosslinkers for Polyurethane Powder Coatings**

- Crelan NI 2 — ε- Caprolactam blocked IPDI prepolymer
- Crelan NW 5 — ε- Caprolactam blocked Desmodur W prepolymer
- Crelan VPLS 2256 — ε-Caprolactam blocked IPDI isocyanurate
- Crelan EF 403 — Emission-free crosslinker based on an IPDI uretdione
Another class of hardeners for polyurethane powder coatings are based on the 4 membered uretdione ring. The uretdione linkage can be thermally cleaved to regenerate the active isocyanate groups.

An oligomeric uretdione (as pictured in Figure 21), of low free monomer content can be thermally cleaved and the liberated polyisocyanate groups then reacted with a solid polyl to form a crosslinked polyurethane powder coating without any blocking agent emissions. Such curing agents are primarily used with hydroxy-functional polyesters or polyacrylates but also in epoxy/polyester hybrid and TGIC/polyester powder coating formulations. Bayer markets a cycloaliphatic polyuretdione hardener for polyurethane powder coatings under the trademark Crelan EF 403.

**Rucote Polyesters**

A wide variety of solid grade hydroxyl functional polyester resins are marketed by Bayer under the Rucote trademark. They are formulated to the glass transition temperature range necessary for the production of storage stable polyurethane powder coatings. They are used in combination with the Crelan hardeners. The Rucote polyesters are available in a range of OH content, functionality, reactivity and exterior durability so that a wide range of coating performance properties are achievable. Polyurethane powder coatings are especially valued for the properties of very high gloss, smoothness and chemical resistance.

**Polyol Coreactants**

**Desmophen Polyols**

A wide variety of polyesters, polyethers, and acrylics are marketed by Bayer under the trademark Desmophen.

Desmophen polyesters are available in grades ranging from highly-branched to linear, from high to low hydroxyl content. In general the product numbers of the different Desmophen products are a clue to the structure - the lower the number, the higher the degree of branching. As the number increases, the polyesters become more linear and have a lower hydroxyl content.

Desmophen C polyols are based on aliphatic polycarbonatediols. Products are available with various compositions and molecular weight variations. Polycarbonatediols are used to formulate polyurethanes with outstanding hydrolytic resistance.

Desmophen polyacrylic resins can be differentiated from the polyesters by the “A” designation before the product number. For example, Desmophen A 160, Desmophen A 365, and Desmophen A 450.
Desmophen polyether polyols are designated by the letter “U” following the number. For example, Desmophen 500U and Desmophen 1600U.

Other Polyether Polyols

Bayer also offers polyether polyols under the trademarks Multranol, Arcol and Acclaim. The Multranol and Arcol polyol families contain a wide range of polyether polyols varying in functionality, molecular weight and composition for applications in coatings, adhesives, sealants and elastomers.

The Acclaim polyols are high-performance low-monol polyethers, prepared with Bayer’s proprietary IMPACT technology, using a patented organo-metallic propoxylation catalyst. The terminal end groups are predominantly secondary and have a relatively low reactivity. Acclaim polyols are used in the formulation of isocyanate-terminated prepolymers, coatings, sealants, adhesives, and elastomers.

Desmolith

Under the trademark Desmolith, Bayer markets a polyether polyol emulsion in water used in combination with Desmodur VL polyisocyanate to produce polyurethane/polyurea polymer concretes especially suitable for applications requiring chemical and thermal shock resistant floor coatings.

Bayhydrol Polyols

Under the trademark Bayhydrol, Bayer markets hydroxyl functional polyurethane, polyacrylic and polyester dispersions developed for the formulation of two component waterborne coatings. When combined with Bayhydur water dispersible polyisocyanates, coatings formulations can be produced that satisfy the performance requirements of a variety of applications including: wood furniture and kitchen cabinetry, automotive plastics and site-applied coatings to wood and concrete floors as well as to exterior metal building panels.

Polyamine Coreactants

The reaction between polyamines and polyisocyanates to form polyureas is well known. Polyurethane polyureas form tough coatings and elastomers of high strength and elasticity. However, the very high reactivity of commercially available aliphatic polyamines with polyisocyanates requires the use of multi-component spray equipment with very accurate metering and effective mixing capabilities. This significantly reduces the potential applications for polyurethane polyureas in coatings.

In response Bayer has developed a number of hindered aliphatic polyamine chemistries and products. The reduced reactivity of these polyamines makes it possible to formulate high solids coatings with a potlife comparable to that of conventional two-component polyurethane coatings.
**Polyaspartic Esters**

The polyaspartic acid esters contain secondary aliphatic amine groups which react readily with isocyanates as shown in Figure 22.

An interesting feature of the aspartic acid ester is that water accelerates the reaction with polyisocyanates. So, the mixed coating may have a relatively long potlife, but it quickly hardens when applied to a substrate and exposed to humidity. The cured coatings can offer high color stability, excellent weathering and corrosion resistance. Properly formulated paints can meet the requirements of SSPC - Paint 39 Specification “Two-component Aliphatic Polyurea Topcoat, Fast or Moderate Drying, Performance-Based”. Through selection of the starting diamine, it is possible to produce a family of products with resultant variations in viscosity and reactivity with polyisocyanates. Under the Desmophen NH trademark Bayer markets a number of polyaspartic acid ester coreactants including: Desmophen NH 1220, Desmophen NH 1420 and Desmophen NH 1520.

**Polyaldimines**

The structure for an aldimine is shown in Figure 23. It’s reaction with an isocyanate is shown in Figure 24.

Because of their low viscosity and reactivity with polyisocyanates, polyaldimines are very well suited as reactive thinners in high solids two component coatings. Bayer markets a polyaldimine coreactant under the trademark Desmophen PAC XP 7076.
Bisoxazolidine Hardeners

In the application of thick section moisture-curing polyurethane coatings, the entrapment of the CO₂ gas can result in bubbles, porosity, and other defects in the film. Bisoxazolidines (Figure 25) are most useful as latent co-reactants for aliphatic polyisocyanate prepolymer in one-component moisture curing systems. Bisoxazolidines contain no functional groups reactive toward isocyanates until they react with water, for example, as found in the atmospheric humidity. The hydrolysis of the bisoxazolidine results in a ring opening to yield an aminoalcohol (Figure 26).
The extent of reaction of the resultant diaminodiol with the polyisocyanate will depend on the stoichiometry of isocyanate to active hydrogen groups chosen (Figure 27).

Bayer markets bisoxazolidine latent hardeners under the trademarks Hardener OZ and Hardener XP - 7179.

**Other Coreactants**

Oils and alkyds can be used with Bayer polyisocyanates. For example, various short oil alkyds can be used with Desmodur HL and Desmodur IL polyisocyanates. Castor oil that contains hydroxyl groups is a potential coreactant for Desmodur L and Mondur MR polyisocyanates.

Desmodur L and Desmodur N polyisocyanates crosslinked with epoxy resins containing secondary hydroxyl groups give films with good adhesion and resistance to aggressive chemicals. Some phenolic resins combined with Desmodur L polyisocyanates give particularly good water-resistant films.

Silicone resins with hydroxyl groups also react with polyisocyanates. For example, Baysilone UD resin reacted with Desmodur L polyisocyanate at room temperature produces coatings which maintain their mechanical properties even after prolonged treatment of the films at temperatures as high as 180°C, although a certain amount of yellowing occurs.

Vinyl polymers containing hydroxyl groups are also suitable coreactants for Bayer polyisocyanates. Such systems can be used for coating wood and plastic.

Other products which are suitable for use with polyisocyanates include styrene allyl alcohol copolymer, cellulose esters, ketone resins, bituminous coal tar, and bitumen.
Waterborne Polyurethane Coatings

The traditional solvent borne polyurethanes have long set the standard for high performance coatings systems. Under the twin demands for high performance coatings and more environmentally favorable alternatives, the development of waterborne polyurethane technologies has offered new solutions to the coatings formulator. Bayer offers various waterborne technologies to meet the performance demands of many industrial coatings applications.

Bayhydrol Polyurethane Dispersions

An aqueous polyurethane dispersion is a colloidal system in which particles of polyurethane are dispersed in a continuous phase (water). The structure of a classical polyurethane dispersion resin type is shown in Figure 28. However Bayer can produce polyurethane dispersions by various technologies.

![Figure 28 Polyurethane-urea resin](image)

Having a choice of production technologies means that Bayer can select the dispersion compositions that will optimize the polymer performance properties for the application rather than one which is limited by a production capability. A key benefit of Bayer’s process capabilities is the ability to produce n-methylpyrrolidone free as well as completely cosolvent free dispersions. Bayer markets a wide range of dispersions for applications in coatings including: rigid and flexible plastics; automotive interior and exteriors; metal primers and exterior building panels; interior maintenance and architectural applicators; wood furniture; flooring and paneling. These include both non-functional and functional dispersions.

Two-Component Waterborne

Bayer offers hydroxyl functional polyurethane, polyacrylic and polyester dispersions for use in two-component waterborne polyurethane coatings. Bayhydrol dispersions are also available containing: fatty acid modification with oxidative drying capability; carboxyl functionality; and unsaturation with radiation curing capability. Bayer thus offers Bayhydrol dispersions capable of further crosslinking by: hydrophilically modified Bayhydur polyisocyanates; substituted melamines; polycarbodimides; polyaziridines; UV and EB radiation (Bayhydrol UV dispersions).

Bayer further markets polyurethane dispersions for textile intermediates under the trademark Impranil and for glass fiber sizings under the Baybond trademark.

Water Dispersible Polyisocyanates

In order to optimize the application and performance properties of two component waterborne polyurethane coatings, it is necessary to develop polyisocyanate curing agents that are more easily dispersible in water. Under the trademark Bayhydur, Bayer markets hydrophilically modified polyisocyanates based on HDI and IPDI that can be readily dispersed into a water-based polyol to give a true two-component polyurethane coating. Just as in the case of the Bayhydrol dispersions, the evolution of the Bayhydur product family results in a continuous development of technical product alternatives. The standard product of today is represented by the idealized structure of Figure 29. In this case a hydrophilic polyether segment is reacted with the hydrophobic polyisocyanate. This reaction takes place readily and can dramatically improve the water dispersibility of the polyisocyanate, but inevitably results in some reduction of isocyanate functionality. Bayer offers a wide range of water dispersible polyisocyanate products, including Bayhydur 302 and 303.
One new approach in development takes advantage of the potential to react an isocyanate with a urethane group to form an allophanate (Figure 30). This synthesis can start with the same basic HDI polyisocyanurate as above but results in a hydrophylically modified polyisocyanate of higher NCO functionality. Development products based on this chemistry are being marketing as Bayhydur VP LS 2319 and Bayhydur VP LS 2336 polyisocyanates.

The Bayhydur product family development continues to grow to support the new application demands for two component waterborne polyurethane coatings.

In addition, under the trademark Bayhydur BL, Bayer markets water dispersible blocked polyisocyanates for one component polyurethane coatings.

**Radiation Curable Technologies**

For the formulation of UV and EB curable coatings, Bayer markets a number of resin technologies under the trademarks Desmolux and Bayhydrol UV. In this way the performance properties that polyurethanes bring to traditional coatings systems including toughness, flexibility, abrasion resistance, and adhesion can be incorporated into radiation curable coatings.

**Desmolux Urethane Acrylates**

Desmolux products include unsaturated aliphatic and aromatic urethane acrylates. These acrylate functionalized polyurethanes (Figure 31) are based on the family of Bayer’s monomeric diisocyanates and polyisocyanates. This results in a family of oligomers offering a wide range of viscosity, functionality and reactivity as well as mechanical and weathering performance properties.
Marketplace applications include:

- Clearcoats for cementitious roof tiles and building façade panels
- Clearcoats for plastic, including polycarbonate twin wall sheetings, as well as for metal rims and wheels
- Automotive repair fillers, primers and clearcoats
- Rigid and flexible plastics including soft-feel coatings
- Wood furniture and parquet finishes

Desmolux Urethane Acrylates For Dual-Cure

Bayer markets Desmolux acrylate functionalized polyisocyanate oligomers which contain both residual active isocyanates and unsaturated acrylate groups. As depicted in Figure 32 such oligomers will undergo UV or EB reactions of the unsaturated functionality in addition to the well known reactions of isocyanates. The isocyanates can react with the available hydroxyl groups of polyols formulated into the system and with hydroxyl (or phenolic) groups on the substrate surface. The latter is a widely practiced technique to improve the adhesion of UV curable coatings to wood substrates, especially on difficult to adhere resinous or oily hardwoods. Excess polyisocyanate groups can also undergo the well-known 'water reaction' (Figure 34) to yield tough, flexible polyurea crosslinks. Such dual-cure systems offer the fast cure and high productivity inherent in the UV curing process, while the polyisocyanate post-curing can provide improvements in:

- shadow cure
- adhesion
- mechanical and chemical resistance properties

Under the trademark Desmophen VP LS 2089, Bayer offers a polyester resin containing both hydroxyl and unsaturated functionality for use in dual-cure coatings systems.
Bayhydrol UV Urethane Acrylate Dispersions

Bayer markets UV curable polyurethane dispersions under the trademark Bayhydrol UV (Figure 33). These high molecular weight dispersions represent a successful marriage of two of the best Green Technologies: radiation curable and waterborne resin technologies.

![Figure 33](image.png) UV curable polyurethane dispersions

To the high productivity of UV curing are added the advantages of:

- Lower photoinitiator content
- Low shrinkage, improved adhesion
- Physical drying
- High elasticity, scratch and abrasion resistance
- Cosolvent and reactive thinner free formulations
- Thin film application potential
- Reliable gloss control
- Easy spray application

Bayhydrol UV dispersions also offer additional formulating flexibility. Although specific compatibility must be evaluated, in principle the Bayhydrol UV dispersions can be blended with other reactive or non-reactive polyurethane and polyacrylate dispersions.

Bayhydrol UV dispersion applications include:

- Wooden millwork, furniture and flooring
- Rigid and flexible plastics including decorative film, PVC flooring and soft-feel coatings
- Paper coatings and leather finishes
- Printing inks and overprint varnishes

Two-Component Coating Systems

The most frequently recommended products for two-component coatings applications are Desmodur N polyisocyanates and Desmophen polyols. In addition, for some applications the Desmodur and Mondur aromatic polyisocyanates may also be appropriate.
Calculations

When preparing two-component coating formulations, the rules for chemical equations are followed. In theory, a maximum molecular weight is reached and those properties associated with molecular weight are optimized when one equivalent of isocyanate reacts with one equivalent of hydroxyl, that is, when the ratio of NCO to OH is 1.0 / 1.0 (Equation 1, Table 3). In practice, a small excess of isocyanate, about 5-10%, is often used to allow for the likely destruction of isocyanate by water contained in solvents and pigments, so that the NCO to OH ration is maintained at 1.0 / 1.0. It is sometimes desirable to vary the NCO to OH ratio from about 0.9 / 1.0 about 1.2 / 1.0 in order to modify the properties of the coating. In any event, it is important that the NCO to OH ratio be controlled.

In order to achieve an NCO to OH ratio of 1.0 / 1.0 the weight of one equivalent of the supplied form of the isocyanate is reacted with one equivalent of the supplied form of the polyol. Usually the product literature will list the equivalent weights, but if not, then the polyisocyanate literature will give the %NCO and the polyol literature will give the %OH or the OH number. The NCO equivalent weight can be calculated from the %NCO (Equation 2, Table 3), and the OH equivalent weight from either the %OH or the OH number (Equation 3, Table 3). These equations can be combined to calculate the weight ratios of ingredients for any NCO to OH ratio. Basic algebra is all that is necessary for these calculations. Sample calculations are shown in Table 4.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Equations for polyisocyanate/polyol reaction</th>
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<tbody>
<tr>
<td>1. n(OCN—R—NCO) + n(HO—R—OH) \xrightarrow{(-C-N-R—N-C-O-R'—O—)} \text{Urethane Polymer}</td>
<td></td>
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<tr>
<td>2. Equivalent weight (Isocyanate-containing resin) = ( \frac{42 \times 100}{\text{% NCO}} )</td>
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| 3. (a) Equivalent weight (Hydroxyl-containing resin) = \( \frac{17 \times 100}{\text{% OH}} \)  
(b) Equivalent weight (Hydroxyl-containing resin) = \( \frac{56,100}{\text{OH Number}} \) |

**Table 4**
Example problems

Determine the amount of Desmodur N-100 polyisocyanate required to react with 300 lbs of Desmophen R-221-75 polyol. Use a 1.2 to 1.0 NCO to OH ratio.

Desmodur N-100 contains 22% NCO  
Desmophen R-221-75 contains 3.3% OH

a) Equivalent weight N-100 = \( \frac{42 \times 100}{22} = 191 \)

Equivalent weight R-221-75 = \( \frac{17 \times 100}{3.3} = 515 \)

For the theoretical reaction, it is necessary to use 1 equivalent or 191 lbs of N-100 with 1 equivalent or 515 lbs of R-221-75.

b) The number of equivalents in 300 lbs of R-221-75 = \( \frac{300}{515} = 0.58 \)

c) At 1.0 to 1.0 NCO to OH ratio, equivalents of N-100 required are 0.58.  
\begin{align*} 
\therefore \text{The amount of N-100} & = 0.58 \times 191 = 111 \text{ lbs} \\
d) \text{Since a reaction ratio of 1.2 to 1.0 of NCO to OH is desired, then the amount of N-100 required is} & = 0.58 \times 1.2 \times 191 = 133 \text{ lbs} \end{align*}
Properties

The properties of a two-component polyurethane coating depend on certain factors, such as the degree of branching of the reaction partners, the content of the reactive groups themselves, and the physical state of the raw materials.

It is possible to change the film properties by using the same polyisocyanate with different polyols while maintaining a constant NCO to OH ratio. Generally speaking, the higher the hydroxyl content of the particular reaction partner, the harder and more chemical resistant the films will be. A low hydroxyl content normally gives softer and more flexible films.

A further possibility for modifying the film properties is to use the same polyol and vary the quantity of the polyisocyanate. By “undercrosslinking,” which means using an NCO to OH ratio less than 1.0 / 1.0, the polyurethane film generally becomes softer and perhaps more flexible, less weather resistant, and less resistant to solvent and chemicals. On the other hand, by “overcrosslinking,” using an NCO to OH ratio greater than 1.0 / 1.0, the resultant films tend to be harder and more chemical resistant. Another possibility for changing the properties of a coating is to use a blend of polyols or polyisocyanates. For instance, a rigid, brittle acrylic urethane coating could be made less brittle and more flexible by blending in a softer, less-branched polyester. Also, a slower drying polyurethane could be made to dry more quickly by blending some faster reacting or faster drying polyisocyanate with the original. For example, blends of Desmodur Z and Desmodur N polyisocyanates are used to take advantage of the faster physical dry of Desmodur Z and the higher chemical crosslinking of the Desmodur N polyisocyanates.

Curing

The curing of two-component polyurethane coating systems can be carried out at room temperature. The drying times can vary considerably depending on the types of polyols and polyisocyanates used. In general, systems based on the following polyisocyanates dry at room temperature in these approximate relative times:

- Desmodur IL: 1
- Desmodur HL: 2
- Desmodur L: 6
- Desmodur N + catalyst: 6
- Desmodur N: 30

Elevated temperatures are often used for forced drying in production line coatings. The highly reactive Desmodur IL and Desmodur HL polyisocyanates have particular importance for baked finishes as they allow extremely short drying times. Coatings based on Desmodur L or Desmodur N polyisocyanates can also be cured at elevated temperatures to reduce the cure time.

Desmodur N aliphatic polyisocyanates have low reactivity by nature and longer drying times can be expected. The incorporation of 0.005% dibutyltin dilaurate, 0.2% zinc octoate, or up to 0.5% Desmorapid PP catalyst based on solid binder reduces the dry time to practical levels.

While coatings based on Desmodur L polyisocyanate normally do not require a catalyst, the addition of an accelerator may be advisable for certain applications. Metal-based catalysts have less of an effect on Desmodur L polyisocyanates than do tertiary amines such as Desmorapid PP catalyst, which is normally used in the range of 0.05-0.2% based on solid binder.

Coatings based on Desmodur IL or Desmodur HL polyisocyanates are normally used without a reaction accelerator.
Application

The chemical curing mechanism of two-component polyurethane coatings makes it necessary to consider the following points:

1. Both components must be mixed together thoroughly.
2. The reaction which begins immediately upon mixing results in a gradual to rapid viscosity increase.
3. The increase in viscosity eventually leads to a gelation of the paint.

The usable potlife depends on the following factors:

- Binder concentration and coating solids level
- NCO/OH ratio
- Polyol and polyisocyanate used
- Catalyst type and concentration
- Temperature of the coating mixture
- Choice and quality of the solvents
- Possible effects of additives, pigments, or extenders

If these factors are taken into account, the potlife of conventional two-component polyurethanes can be set to be one work shift. In principle, this means any application method can be employed. Faster curing coatings require an adjustment in the application method.

Two component polyurethane coatings can be applied by a variety of methods. Application by air, airless, or air-assisted airless spray, electrostatic spray, brush, roller coating, and curtain coating is possible. Careful formulation is required to maximize the application characteristics of each formulation for its end use.

Moisture-Curing One-Component Coatings

Adducts of diisocyanates or polyisocyanate/polyol combinations with an excess of isocyanate groups (prepolymers) can crosslink with atmospheric moisture (Figure 34) to give insoluble higher molecular weight polyurethane/polyureas. This reaction describes the curing principle for moisture-curing polyurethane coatings.

![Figure 34 Polyurea formation (Moisture Cure Reaction)]

There are two ways of formulating one-component coatings of this kind:

a) Preparation of prepolymer from suitable polyisocyanates and polyols
b) Use of Desmodur E polyisocyanates

Prepolymers from Polyisocyanates and Polyols

Desmodur N (HDI), Desmodur L (TDI), and Mondur MR and MRS (MDI) polyisocyanates are suitable for preparing prepolymer used in formulating one-component moisture-curing coatings. The prepolymer are usually prepared from polyols of low functionality and a corresponding stoichiometric excess of polyisocyanate. A moisture-curing clear varnish can be made as follows: The polyisocyanate and solvent
are mixed for a short time in a dissolver, being sure that moisture is excluded. If a moisture scavenger is required, paratoluene sulfonyl isocyanate (pTSI) can be added. After this, the polyol, other additives, and accelerators are added and the mixture is packed in a dry, airtight container. The coating reaches its final viscosity in approximately seven days. The storage stability of the final product is dependent on the polyol used and should be closely examined.

**Desmodur E Polyisocyanates**

The trademark Desmodur E covers a range of ready-to-use polyisocyanates for one-component coatings which may require no other compounding when used in clear coatings except for the addition of solvent where necessary.

**Properties of Moisture-Curing One-Component Coatings**

The properties of moisture-curing one-component coatings are principally determined by the nature of the particular base isocyanates used. For example, one-component coatings based on aliphatic isocyanates (HDI, IPDI, Desmodur W diisocyanate) generally need longer drying times than those based on aromatic isocyanates (TDI, MDI). The drying times depend not only on the temperature, but also on the amount of atmospheric moisture present. With very low absolute moisture content, the drying times may be increased. The aliphatic polyisocyanate based moisture-cured coatings often require metal catalysts (such as dibutyltin dilaurate) to provide reasonable cure times.

The weathering properties of one-component coatings also largely depend on the type of isocyanate used. Coatings based on TDI or MDI have a tendency to yellow in the light and show a relatively rapid loss of gloss on weathering. Those based on HDI, IPDI, and Desmodur W diisocyanate are light stable. Depending on the composition, these one-component coatings may be equivalent in gloss retention and chalk resistance to two-component polyurethane coatings based on Desmodur N polyisocyanates. One-component polyurethane coatings have very good mechanical properties.

The films can range from hard to very flexible. Surfaces are particularly mar resistant and abrasion resistance is exceptionally high. The films also have good resistance to chemicals, including the stronger organic acids, as well as, alkalis, alcohols, solvents, and water.

Aliphatic polyisocyanate based moisture curing resins are available which can be formulated into coatings which meet the requirements of the SSPC - Paint 38 Specification “Single-Component Moisture-Cure, Weatherable Aliphatic Polyurethane Topcoat, Performance-Based”.

**Pigmented One-Component Coatings**

Due to the sensitivity of one-component coatings to moisture, a special technique has to be followed when formulating pigmented coatings. This involves the use of pTSI, Additive OF, and splitting the grind procedure into several steps. This process may be accomplished in the same amount of time as the milling of a conventional coating and can be done with the same equipment. The formulation is divided into four operations:

1. Weighing
2. Predispersing
3. Dispersing in the sand mill
4. Filling
As explained in Figures 35 and 36, the individual components are weighed in the given sequence and predispersed with a dissolver. In so doing, two processes occur simultaneously:

a) Homogenization of the weighted materials
b) Dehydration of the pigments, extenders, and solvents by pTSI

Carbon dioxide is released through the chemical reaction between water and pTSI, acting as a buffer gas preventing contact with air and humidity. While the dissolver charge is warm, it can be dispersed in a sand mill.

After cooling, the catalyst, and if necessary Additive OF, can be added and the batch adjusted to the desired viscosity with anhydrous solvents. The material should then be packed in dry airtight containers.

Another method of formulating pigmented one-component coatings is to add the pigment in the form of a pre-dispersed paste colorant. In this case, the pigment mill base can be prepared in a binder which reacts as little as possible with the NCO group. The incorporation of pTSI ensures that the pigment paste is free of water. The paste may then be mixed with Desmodur E polyisocyanate binders such as Desmodur E-28.
Curing

The drying rate of one-component coatings is dependent on the relative atmospheric humidity and the temperature. Low temperature and low atmospheric humidity may slow down the drying considerably.

As with two-component systems, one-component coatings based on aliphatic polyisocyanates often require the incorporation of reaction accelerators. Metal compounds such as dibutyl tin dilaurate are especially suitable for this purpose.

Application

Moisture-curing coatings based on the Desmodur E polyisocyanates are normally applied by brushing or spraying. Dip coatings and curtain coating cannot generally be used because of the extended contact between the liquid coating and atmospheric moisture.

Unpigmented one-component coatings are used primarily for wood substrates such as parquet flooring and other indoor wood flooring applications. Another area of application is for the sealing or coating of concrete floors, and decorative seamless floors.

Pigmented one-component coatings can be used for anticorrosion coatings for metal, for the coating of concrete substrates, and for various other decorative and protective coatings.

Formulating Aids

Modifiers

In addition to the main resin components, one- and two-component polyurethane coating systems frequently contain other modifying ingredients. These are added to improve specific application properties (leveling agents or thickeners, for example), and are normally incorporated as a small weight percentage of the total binder. For certain applications, it may be best to formulate coatings with a high percentage of a modifying binder or resin component. Products such as a cellulose acetate butyrate, low molecular weight acrylic resins, and polyvinyl chloride/polyvinyl acetate (PVC/PVAC) copolymers are suitable modifiers.

Solvents

Suitable solvents for one- and two-component systems include esters, ketones, and ether esters. Possible diluents are aromatic hydrocarbons such as toluene, xylene, or higher boiling fractions. Desmodur Z polyisocyanates are compatible with paint systems containing aliphatic hydrocarbons such as VM&P naphtha. Chlorinated hydrocarbons may be used only if there are no finely divided metal additives in the coating. The choice of solvents and diluents should be evaluated for each coating system.

Should it be necessary to dilute polyisocyanates, special care should be taken when selecting the solvents. Any solvent chosen must not contain hydroxyl groups. This means that no alcohols or solvents contaminated with water should be used. It is not recommended to dilute polyisocyanates below 35% solids since precipitation may occur.

The water content of the solvents or solvent blends used for diluting polyisocyanates should not exceed 0.05% (500 ppm). Urethane grade solvents are generally suitable for polyols and polyisocyanates.

Solvents which contain reactive groups such as amines should not be used since they react with isocyanate groups.

Regulations and safe handling procedures governing flammable and combustible liquids must be followed.
Pigments and Extenders

The following inorganic pigments are suitable for most two-component polyurethanes:

- **White:** Titanium dioxide
- **Yellow:** Iron oxide yellow, nickel and chrome titanates, chrome and cadmium yellows
- **Brown:** Iron oxide brown
- **Red:** Iron oxide red, cadmium red
- **Black:** Iron/manganese mixed metal oxide black, iron oxide black, some carbon blacks
- **Blue:** Mixed metal oxide blue
- **Green:** Chrome oxide green

A marked reduction in potlife may be expected when using the following pigments: zinc oxide, red lead, and some carbon blacks. Zinc phosphate has gained special importance as a corrosion inhibitor, but may shorten the potlife also. Zinc dust and non-leafing aluminum may be used for anti-corrosion primers and non-leafing aluminum types in barrier type primers.

The following organic pigments are suitable:

- **Blue:** Phthalocyanine blue
- **Green:** Phthalocyanine green
- **Red:** Perylene and quinacridone red
- **Yellow:** Monoazo, isoindoline, monoarylide yellow

Other classes of organic pigments may be suitable. Some organic pigments may catalytically accelerate the curing reaction of polyurethanes because of their metal content. Potlife studies should be done in systems containing organic pigments. Because of their transparency, some organic pigments will not give sufficient coverage in single-coat applications.

In addition to transparent pigments, soluble dyestuffs can be also used to obtain transparent shades. Soluble dyestuffs generally do not have the same lightfastness as suitable organic pigments. Metal complex dyestuffs can also be used.

Conventional extenders for one- and two-component systems are typical of those used in other types of coatings and include barytes, calcium carbonate, talc, kaolin, mica, precipitated and amorphous silica, and various other silicate types.

Flattening Agents

The incorporation of conventional flattening agents based on silica allows any desired level of gloss to be obtained, either with clear or pigmented two-component polyurethane coating systems. Incorporating polyolefin wax is also advantageous. Micronized polypropylene waxes can be incorporated without difficulty and improve the appearance of the matted surface. In the case of readily dispersible products, it is sufficient to mix in the flattening agent by simple high-speed stirring.

To obtain a matte or eggshell gloss effect, 4-15% flattening agent, calculated on binder, is generally required. This amount will vary depending on the choice of polyol and the mill base composition.

Leveling Agents

Apart from the choice of solvents, adding suitable leveling agents can improve the flow properties when needed.

Cellulose acetate butyrate or low molecular weight acrylic resins are used at levels of 0.2-2.0% calculated on solid binder. The level depends on compatibility with the binder.
Polyvinyl acetate, copolymers of PVC/PVAC, and some urea resins may improve leveling properties when used at levels of 0.5-3.0% calculated on solid binder. Silicone and polymeric fluids and fluorochemical additives can improve flow by lowering the surface tension of the coating material.

**Thickening Agents**

Certain application methods such as curtain coating require increased viscosity of the polyurethane coating system. Suitable thickening agents are copolymers of vinyl chloride and vinyl acetate, precipitated silicas, and bentonite clay.

If an increase in viscosity is desired, copolymers of vinyl chloride and vinyl acetate can be added to the polyol solution in quantities of 5-10% based on solid binder.

Precipitated silicas increase the viscosity and also provide thixotropy. An addition of 3% is often adequate and has only a minor influence on the gloss level. These products are best suspended with solvents in a dissolver before use.

Bentonite clay thickeners are used in additions of up to 1.5% on solid binder to prevent the settling of pigments and extenders. These agents are best suspended with solvents into a gel before use.

When selecting thickeners and pigment suspending agents, their compatibility with polyols must be considered. Additions that adversely affect the characteristic properties of the polyurethane coatings should be avoided.

**Air Release Agents**

Air release agents are particularly useful for the prevention of blistering during application by brush or roller coating. Modified polysiloxanes and other types of polymeric additives are commonly used as defoamers and air release agents. Very careful screening should be done to avoid gloss loss problems which may occur when using too high levels of these additives.

**Catalysts**

Catalysts are used in one- and two-component polyurethane coatings to shorten the curing time, especially in those containing Desmodur N aliphatic polyisocyanates. Various metal compounds such as dibutyl tin dilaurate and zinc octoate are commonly used catalysts in both two-component coatings and one-component moisture-curing types. Desmorapid PP catalyst, a long chain tertiary amine, is also used in two-component systems. While accelerating the cure of two-component polyurethanes, the use of a catalyst will also shorten the potlife. Excessive catalyst levels can also have a detrimental effect on film appearance, property development, and on exterior durability.

**Storage**

Particular care must be given to the storage of any material containing isocyanate groups. Containers of these products must be kept tightly sealed since their reaction with atmospheric moisture leads to an increase in viscosity and eventually gelation. Since carbon dioxide is a product of the reaction of isocyanates with water, pressure build-up and possible rupture of sealed containers of water-contaminated polyisocyanates can occur.

Containers used to store polyisocyanates should be inspected prior to use to be certain they are clean and dry.

Moisture should also be excluded from stored polyester, polyether, or acrylic coreactants. Most of these materials are hygroscopic and will absorb and retain moisture. Water contamination of the polyols may lead to inferior film properties of the finished coatings.

All legal regulations concerning the storage of Bayer products must be observed.
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