photos : ginlo-photo.com

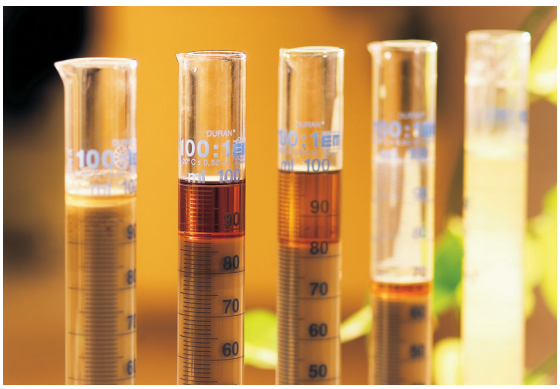
Hand Moulding
Hand processing of cast polyurethane systems

covestro

Short overview on polyurethane

Presentation

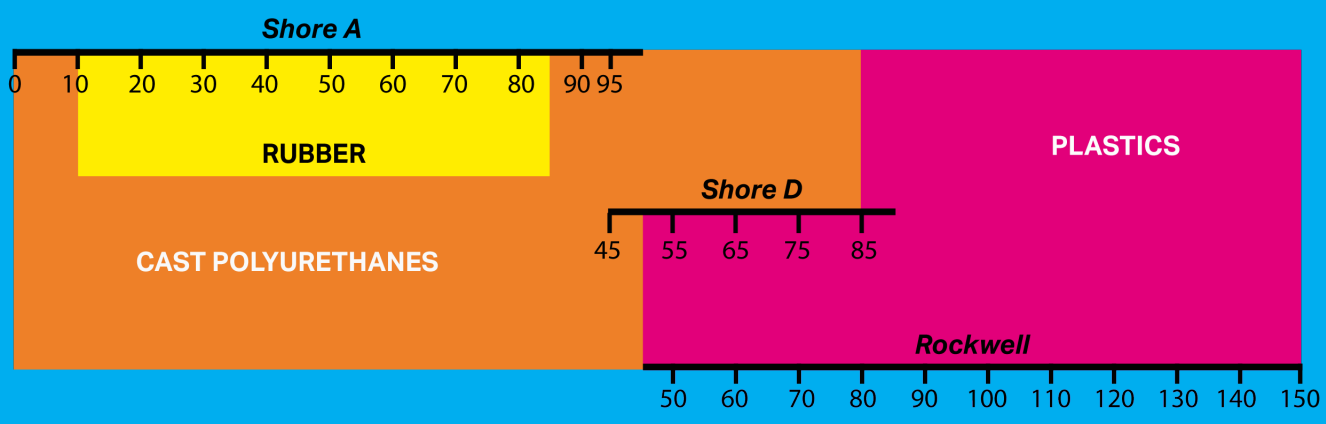
In 1937, a new category of polymers called polyurethanes was developed by Otto Bayer. The polyaddition reaction of a broad variety of raw materials proved a versatile method to produce customized plastics. This discovery was rapidly adapted and modified by many industrial chemists, so that by the 40s, the possibility to develop polyurethane systems with elastomeric properties was already recognized. This new material appeared to be very promising: soon polyurethane parts were manufactured, replacing rubber in many applications. A wide range of properties can be obtained with polyurethanes by changing the raw materials and formulations. Polyurethane elastomers distinguish themselves from other elastomers (such as rubber and silicone) by their wide range of hardnesses (refer to Exhibit 1), high abrasion resistance and load bearing capabilities.



Preamble

A polyurethane elastomer is made up of alternating soft and hard segments resulting from the reaction of at least three basic components : a diisocyanate, a long chain polyol and a short chain extender. Many different polyurethane elastomers can be made by changing the sequence of the reactive components. Covestro concentrate the efforts in the development of the prepolymer and the quasi prepolymer processes (briefly described hereafter). The prepolymer process enables to work either at room temperature or at high temperature (around 80°C) while the quasi prepolymer systems are processed at lower temperature (around 45°C).

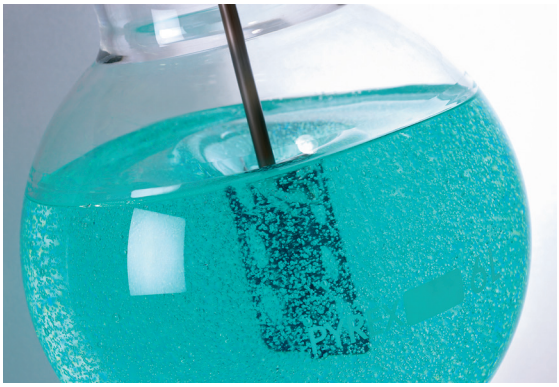
Exhibit 1 : Hardness range



Prepolymer process

Prepolymer generation

Initially, diisocyanate and polyol react together and link with urethane functions to constitute a prepolymer (refer to Exhibit 2). The prepolymer is usually either a thick viscous liquid or a low-melting-point solid with terminal isocyanate functions (-NCO).



Desmodur® prepolymers are mostly obtained by the reaction of toluene diisocyanate (TDI) or diphenylmethane diisocyanate (MDI) and various long chain polyether or polyester polyols.

Among all the polyether polyols, polypropylene glycol (PPG) and polytetramethylene ether glycol (PTMEG) are the most usual ones. The main polyester polyol families developed by Covestro are polyadipate and polycaprolactone.

The chemical composition and the molecular weight of the polyol determine the structure of the soft segment and generally the properties of the end product.

Chain extender curing

The formulated prepolymer is cured with short chain extenders that are either diols, such as butanediol (Baytec® XLB) or diamines, such as methylene-bis chloroaniline (MOCA), to form the polymer. The short chain extender reacts with the prepolymer to form urethane or urea functions that constitute the hard segment of the polymer (refer to Exhibit 3).

The mix remains workable for a few minutes (during the "pot life") and then hardens to become a solid elastomer.

High temperature curing (around 100°C) generates a three dimensional structure due to the cross-linking of the polymer chains. For cold curing systems, the crosslinking is achieved by a several days resting of the moulded parts. This step confers the elastic properties to the end product.

Exhibit 2 : Prepolymer formation

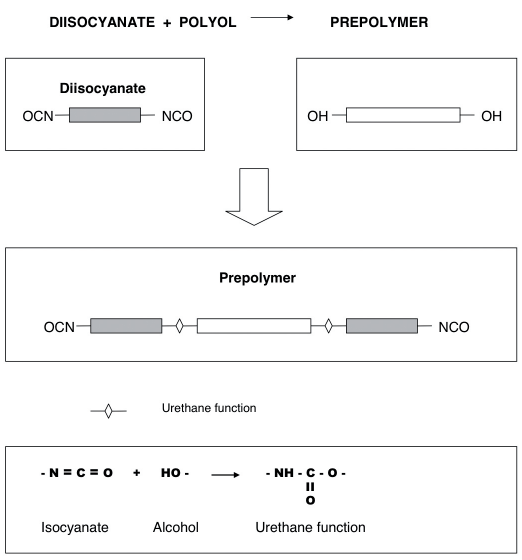
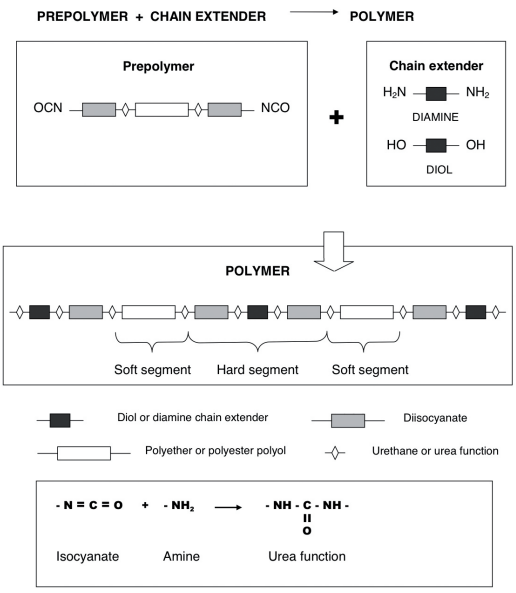


Exhibit 3 : Polymer formation



Quasi-prepolymer process

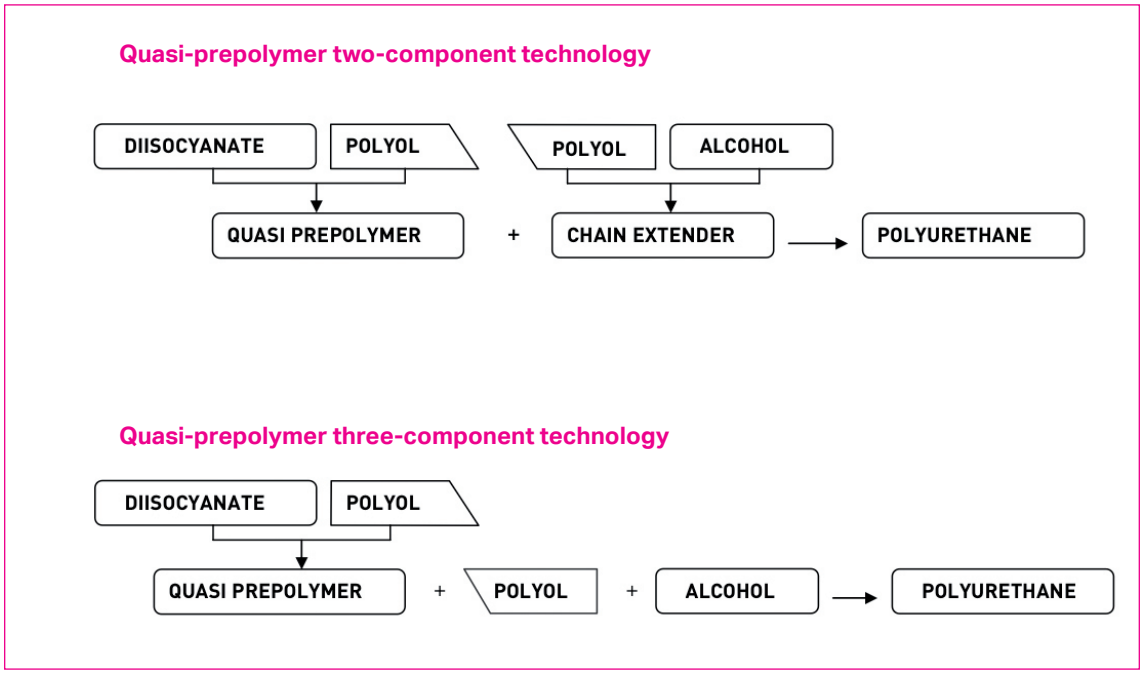
Made from MDI isocyanate and polyether or polyester based polyol, depending upon the requested properties, these systems have in common their structure and their high flexibility in producing simultaneously a wide range of elastomers.

The quasi prepolymer contains less polyol and has therefore a higher NCO content than a classical prepolymer. The polyol «missing» in the quasi prepolymer will be added either to the alcohol chain extender (two-component version), or as a separate component (three-component version). Please refer to the Exhibit 4 (next page).

The three-component version has got a considerable advantage due to the range of hardnesses it covers with the same components.

Covestro propose several quasi prepolymer systems with high performances.

Exhibit 4 : Quasi-prepolymer technologies



Hand processing procedure

Numerous Desmodur® cast polyurethane systems can be processed by hand, without dispensing machine. Obviously, the longer the pot life, the easier the processing. But skilled operators having an adapted equipment can successfully use systems with a pot life of around 2 minutes.

Most of the time the quantity of product corresponding to a batch is rather small in order to have an efficient mixing. When a large quantity of product is requested to fill a mold and if the pot life is short, it is necessary to make several mixing operations simultaneously.

The following section details the adequate tooling, the weight calculation and the processing procedure step-by-step.

Main equipment

A scale having a capacity compatible with the quantities to be processed and a sufficient accuracy (i.e. 1/100 g).

A container which volume is a least twice that of the total mix to be processed.

A vacuum chamber able to reach an absolute pressure lower than 5 mbar, equipped with a looking-glass and valve to set at atmospheric pressure.

For hot casting systems : two ovens are required, one to preheat the components and another one to heat the mold, cure and post cure the part.

To process the amine pellets such as MOCA, a melting equipment is necessary : MOCA's melting point is 110°C.

A mixer with pneumatic or electric motor (around 3000 RPM), equipped with a disc turbine.

The turbine is made out of a metal rod (around 500 mm long) ended with a disc perpendicularly soldered. For an efficient mixing, the diameter of the turbine should be 1/5 up to ½ of the container diameter. It is driven by a drill machine (at about 3000 – 3500 RPM). Prepare several turbines.

An efficient mixing without creation of vortex is advisable in order to avoid turbulence and generation of bubbles. The turbine should not reach the surface when running. It should touch the bottom of the container with a circular movement.

Additional equipment

Gloves adapted for contact at high temperatures
Safety glasses
A chronometer
A temperature probe
An air dust mask
A brush for the release agent
A piece of rag or an air gun
A hammer with a soft head and a screwdriver.
A narrow spatula

Weight calculation

For each system, a defined ratio of all components is required to achieve the polyurethane with its specific hardness and properties. The numbers of parts have to be converted in weight. To do so, refer to the technical data sheet in order to get the components number of parts and refer to the automatic weight calculation tool (available on request).

The additives (color pigments, anti-hydrolysis, anti-static…) ratios are given as a percentage of the total mix weight except for the catalyst ratio which is given as a percentage of the chain extender weight. The weight calculator takes care of this issue.

Processing procedure

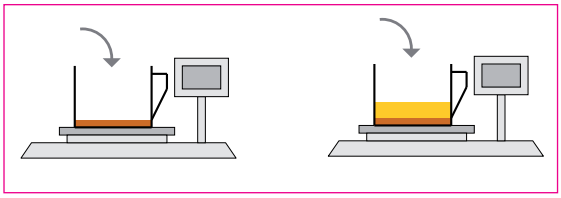
Preparation

Preheat the components at the temperature recommended in the technical data sheet. Coat the mould with a release agent such as silicone, wax or PTFE using a brush. Remove the excess of release agent using a piece of rag or an air gun.

Assemble the mould and put it in the oven at the required temperature. Put the insert (if any) in the oven at the same temperature than the mould.

Weighting

Calibrate the scale before adding each component (reset the scale after each component pouring).



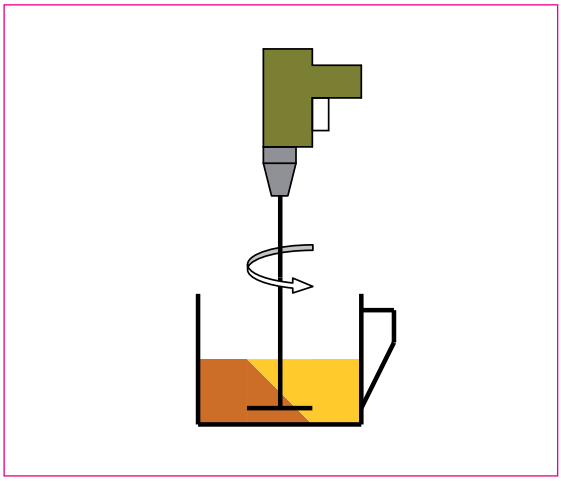
For a two-component system, add first the exact quantity of prepolymer, then the chain extender. Before adding the chain extender, homogenize it vigorously with a turbine (around 10 minutes).

For a multi-component system, begin with the polyol in which will be mixed the smaller quantities (catalyst, anti-foam, Baytec® XLB…). Then add the right quantity of prepolymer.

Start the chronometer as soon as all components are poured together.

Mixing

If the pot life is short, put a small quantity of degassing agent in the container. Mix with the turbine, leaving it dipped into the product (to minimize the generating of bubbles) and making circular movements along the sides.



Duration :

- 30 to 45 sec (up to 2 kg)
- 1 to 1,5 min (over 2 kg).

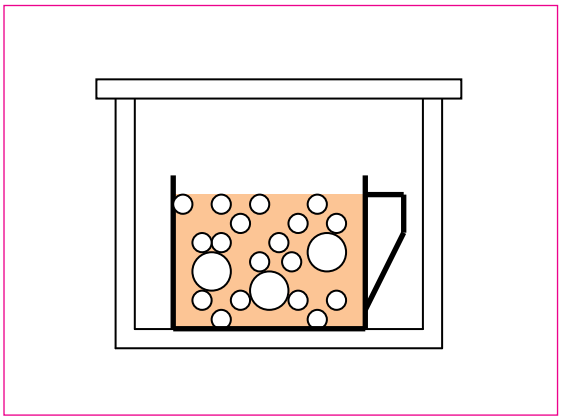
Stop and scrape the walls of the container with a spatula and stir again for 10 seconds. Plunge the turbine in a degreasing solvent after each mixing to clean it for the next coming use.

To be able to use a cleaned turbine, better prepare several ones always remaining in solvent (in Methylene Chloride or any other solvent) and carefully dry a clean one just before setting it on the mixer.

Degassing

Before casting the material into the mould, it is necessary to degas the mix, otherwise bubbles sometimes remain in the end product. To get rid off the bubbles, use a vacuum chamber. Covestro developed a handmix degasser especially designed for hand processing (refer to the technical data sheet available upon request).

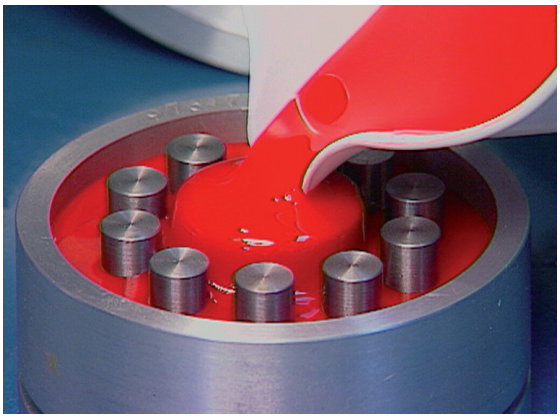
Place the container into the vacuum chamber (vacuum: minus 1 bar) and start degassing taking care the material does not overflow (volume in the container can double). Stop degassing when the level has come back to normal : only some bubbles are left on the surface.



For systems difficult to degas such as viscous mix or with a short pot life, it is recommended to degas the components separately before mixing, in order to decrease the degassing duration.

Casting

Check the temperature of the mould (and the insert) on all sides thanks to a temperature probe before casting.
Pour the degassed mix along the sides of the heated and coated mould. If possible, the mould shall already be in the oven. If not, put the filled mould into the oven at the temperature used to preheat the mould.



Demould after the required time given on the technical data sheet using, if necessary, the screwdriver to open the mould and the hammer to eject the moulded part.

Take care not to harm the polyurethane part. If the part is difficult to demould, blow some air to refresh it.

Post-curing

Post cure the polyurethane parts, if necessary, at the required conditions.

Insert preparation

When the mold includes an insert part, it has to be treated following the steps briefly described below.

First degreasing

In order to remove all dirty particles on the insert, Covestro recommend to degrease it with a solvent for metal degreasing. For a degreasing in vapor phase, leave the insert during 3-5 min. Wait then 10 minutes before grit blasting.

Among the various solvents available, Covestro recommend the following degreasing solvent: Methylene Chloride, Methyl Ethyl Ketone (MEK)or Acetone...

Other methods are available :
Brushing degreasing solvent on the insert or plunging the insert in liquid solvent (leave the insert during 10 min).

Be sure that the solvent is clean enough to degrease properly.

Grit blasting / sand blasting

Grit blast the part of the insert that has to glue with the polyurethane in order to maximize the bonding surface. The sand or grit should be blasted at a pressure of 4 to 5 bars.

The blasting angle and the hammering rate determine the final surface shape : the sand or grit should preferably be an angular cast iron grit whose roughness Ra must be above 12µm.
Among the various grit available, the choice depends on the nature of the insert.

For any details, Covestro remain at your disposal.

Second degreasing

Degrease once again during 3-5 minutes in vapor phase for an optimal efficiency of the bonding agent. Be aware to always use clean solvent.

Wait 10 minutes before applying the bonding agent. Always keep away from moisture, oil and even hand-touching on the blasted surface.

Bonding agent applying

Brush or spray a first layer of bonding agent.
Wait 30 minutes before applying the second layer.
It may be necessary to apply several layers for some specific applications.

Bonding agent can be proposed for cold and hot curing system. It should be diluted at 50% with solvent.

Activation

The bonding agent is activated by heating (refer to the Technical Data Sheet of the bonding agent), generally 1 hour at 100°C.

Auxiliary products

Beside the basic polyurethane components, several products are necessary or available to process cast elastomer systems. In many cases, these additional products are critical for the success of processing : Covestro developed an expertise in PU molding and experienced these products. Covestro's know-how remains at your disposal for all kinds of advice.

Release agent

Enable an easy demoulding of the part. To be applied homogeneously on the surface of the mould before casting. Among the many release agents available, Covestro recommend silicone based ones as they are adapted for all kinds of polyurethane and many applications.

Catalyst

Catalysts are often used to moderate the kinetic reaction, i.e. to control the pot-life and the curing time. As catalysts are part of the systembformulation, please refer to Covestro for any inquiries.

Color pigment

It is very easy to color cast elastomers, especially with liquid color pigments. Covestro remain at your disposal for any details or references.

Fillers

Cast elastomers easily tolerate fillers. The choice of their nature and rate generally depends on the application as fillers modify the properties of the resulting part.

Bonding agent

There are several kinds of bonding agents especially designed for cast polyurethane. Each of them is adapted to some specific process (depends on the substrate and polyurethane system). Please refer to Covestro for details and references.

Degassing agent

For hand casting, a way to make the degassing easier is to pour a small amount of degassing agent into the mix. It reduces degassing time and as a consequence enables to process systems with a short pot-life.

System technical data sheet example

The first side details the raw material characteristics and final properties information. It describes the chemical nature and characteristics of the components, all the mechanical properties of the resulting elastomer.

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DESMODUR® MDQ23165 + BAYTEC® D22-70MF + BAYTEC® XL B (Catalyst SD6-2)

55 Shore A to 55 Shore D

NATURE OF COMPONENTS

Prepolymer nature	Nature of chain extender and other components	
MDI - Ester	BAYTEC® D22-70MF	Ester formulated polyol
	BAYTEC® XL B	Alcohol chain extender

CHARACTERISTICS OF COMPONENTS

	Unit	DESMODUR® MDQ23165	BAYTEC® D22-70MF	BAYTEC® XL B
% NCO	%	16.40 (± 0.2)	-	-
Physical appearance at room temperature	-	liquid	solid	solid
Processing temperature	°C	35	70	35
Viscosity at processing temperature	cps	1000	650	50
Specific gravity at processing temperature	-	1.17	1.17	1.01

ELASTOMER OPTIMAL PROPERTIES (DATA GIVEN AS AN INDICATION)

Prepolymer			DESMODUR® MDQ23165									
Chain extender			BAYTEC® D22-70MF + BAYTEC® XL B									
Hardness at 20°C	**DIN 53505**	**Shore**	**55 A**	**60 A**	**65 A**	**70 A**	**75 A**	**80 A**	**85 A**	**90 A**	**95 A**	**55 D**
10% Modulus	DIN 53504	MPa	0.6	0.8	0.9	1.2	1.5	1.7	2.3	3.0	5.6	13.4
100% Modulus	DIN 53504	MPa	1.7	2.5	3.0	3.9	4.8	5.5	6.8	8.2	11.6	16.2
200% Modulus	DIN 53504	MPa	2.2	3.5	4.3	5.9	7.1	8.3	10.0	11.4	14.2	17.1
300% Modulus	DIN 53504	MPa	2.9	5.0	5.9	8.6	10.1	11.7	13.4	15.6	16.9	18.8
Tensile strength	DIN 53504	MPa	41	46	48	50	43	47	48	57	39	33
Elongation at break	DIN 53504	%	625	600	600	600	600	585	600	600	625	600
Tear strength : without nick	ISO 34-1	kN/m	40	57	63	76	84	90	105	107	130	144
Tear strength : with nick	ISO 34-1	kN/m	23	33	35	38	38	41	50	58	86	117
Resilience	DIN 53512	%	50	50	48	44	43	42	42	40	39	38
Abrasion loss	ISO 4649	mm³	35	35	35	40	40	45	50	50	50	45
Compression set (22 h / 70 °C)	ISO 815-1	%	35	31	39	24	26	26	22	21	31	-
Hardness at -5°C	DIN 53505	Shore	61 A	68 A	72 A	77 A	82 A	86 A	90 A	93 A	97 A	63 D
Hardness at 80°C	DIN 53505	Shore	48 A	56 A	62 A	66 A	71 A	75 A	82 A	87 A	92 A	51 D
Specific gravity			1.20	1.22	1.23	1.23	1.24	1.24	1.24	1.25	1.25	1.26

Labelling : This system data sheet is only valid in combination with the corresponding components current safety data sheets ! Any updating of safety relevant information – in accordance with EU directives – will only be reflected in the Safety Data Sheets, copies of which will be revised and distributed. For further technical information relating to safety, the Safety Data Sheets should be consulted.

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The second side details all the processing data. It describes the storage precautions, the requirements regarding the process preparation, the formulation characteristics and the moulding parameters.

DESMODUR® MDQ23165 + BAYTEC® D22-70MF + BAYTEC® XL B (Catalyst SD6-2)

55 Shore A to 55 Shore D

STORAGE AND USE PRECAUTIONS				
	Unit	DESMODUR® MDQ23165	BAYTEC® D22-70MF	BAYTEC® XL B
Optimal storage temperature of the drums	℃	< 30	< 30	< 30
Storage time (sealed drum)	Month	12	12	12
PREPARATION BEFORE PROCESSING				
Preheating time / preheating temperature	hr / ℃	12 / 45	48 / 80 *	12 / 35
Homogenization before processing required	-	no	yes	no
Degassing required	-	yes	yes	no

Keep from heat and protect against moisture.

PROCESSING											
Prepolymer		DESMODUR® MDQ23165									
Chain extender		BAYTEC® D22-70MF + BAYTEC® XL B									
Hardness	**Shore**	**55 A**	**60 A**	**65 A**	**70 A**	**75 A**	**80 A**	**85 A**	**90 A**	**95 A**	**55D**
Prepolymer processing temperature	℃	35									
BAYTEC® D22-70MF processing temperature	℃	70 *									
BAYTEC® XL B processing temperature	℃	35									
Parts by weight of prepolymer		**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**
Parts by weight of BAYTEC® D22-70MF		**220**	**190**	**160**	**130**	**115**	**100**	**80**	**70**	**50**	**30**
Parts by weight of BAYTEC® XL B		**7.3**	**8.7**	**10.0**	**11.4**	**12.0**	**12.7**	**13.6**	**14.1**	**15.0**	**15.9**
SD6-2 % / total (by weight), (catalyst at the head)	%	**-**	**-**	**-**	**-**	**-**	**-**	**-**	**0.15**	**0.23**	**0.30**
MOLDING AND CURING											
Mold temperature	℃	80							100		
Pot life (400g mixture in a non heated pot)	min	5'	5'	5'30"	5'30"	5'30"'	6'	5'	3'30"	3'	2'30"
Demolding time	min	30'	30'	30'	30'	30'	30'	30'	30'	30'	45'
Post-curing	hr - ℃	16 – 80 **									

* Both the preheating and processing temperatures mustn't exceed 80℃, in order not to destroy irrevers ibly the process qualities of the system.

** For specific applications (optimisation of dynamical properties or massive parts), please consult our Sales Department for additional information on post-curing conditions.

Use of degassing agent is recommended for hand casting.

A 5 weeks aging at room temperature is required to obtain the optimal properties of the elastomer.

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