degussa.

Fine Chemicals

Dyhard®

Make the best links with Dyhard products

The Fine Art of Fine Chemicals.®

Pharma
Agro
Non-Life-Science

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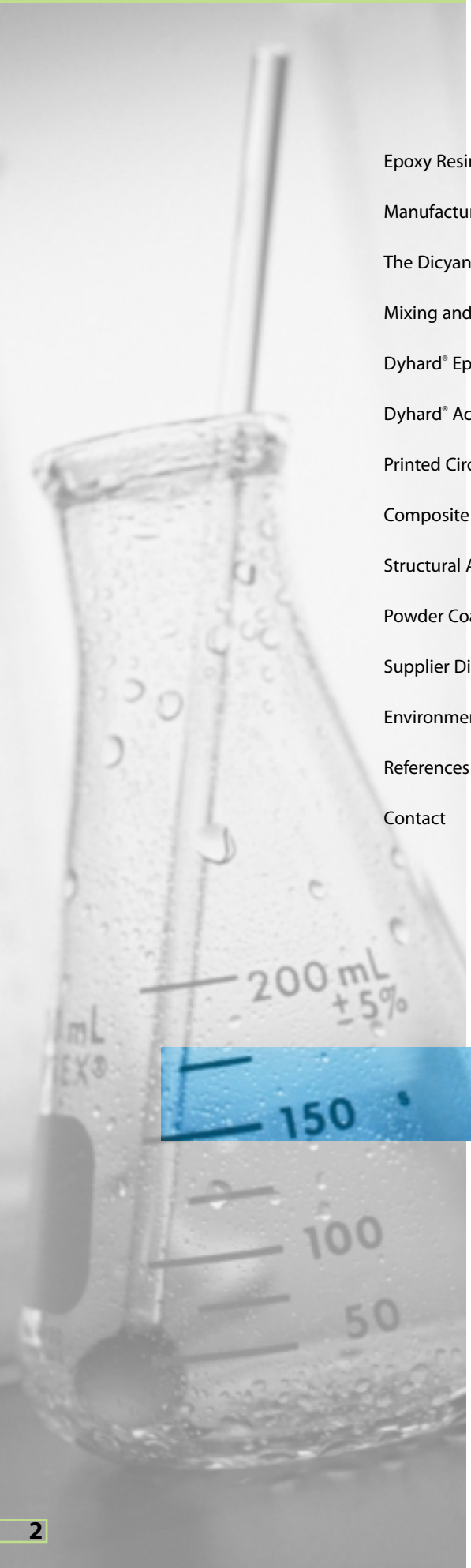
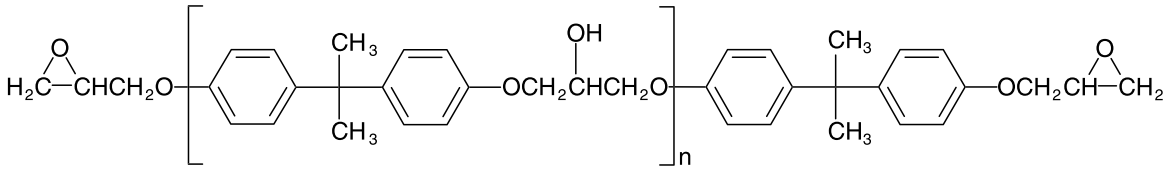


Since epoxy resins were introduced to the market in the 1950s, they have found a large variety of applications in adhesives, casting compounds, composite materials, electrical laminates and coatings [1,2,3].

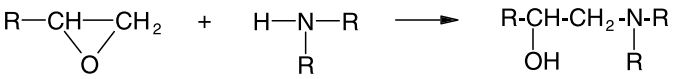
Epoxy resins possess high chemical and thermal stability, coupled with excellent mechanical and electrical properties. The vast majority of commercially used epoxy resins are derived from glycidyl ethers of bisphenol A.



Depending on the degree of polymerization, liquid (n = 0 – 0.5), semisolid (n = 1) or solid (n = 3 – 12) epoxy resins are formed. In applications where intrinsic flame resistance is required, semisolid resins based on tetrabromobisphenol A are used.

Epoxy resins are characterized by their epoxy equivalent weight (EEW). This is the weight of a resin quantity containing exactly 1 mole of epoxy groups.

In the reaction with a hardener, the meltable epoxy resin is converted to a crosslinked thermoset solid. The most important industrial hardeners contain active NH groups, which form 2-hydroxy amine units with epoxy groups in an addition reaction.



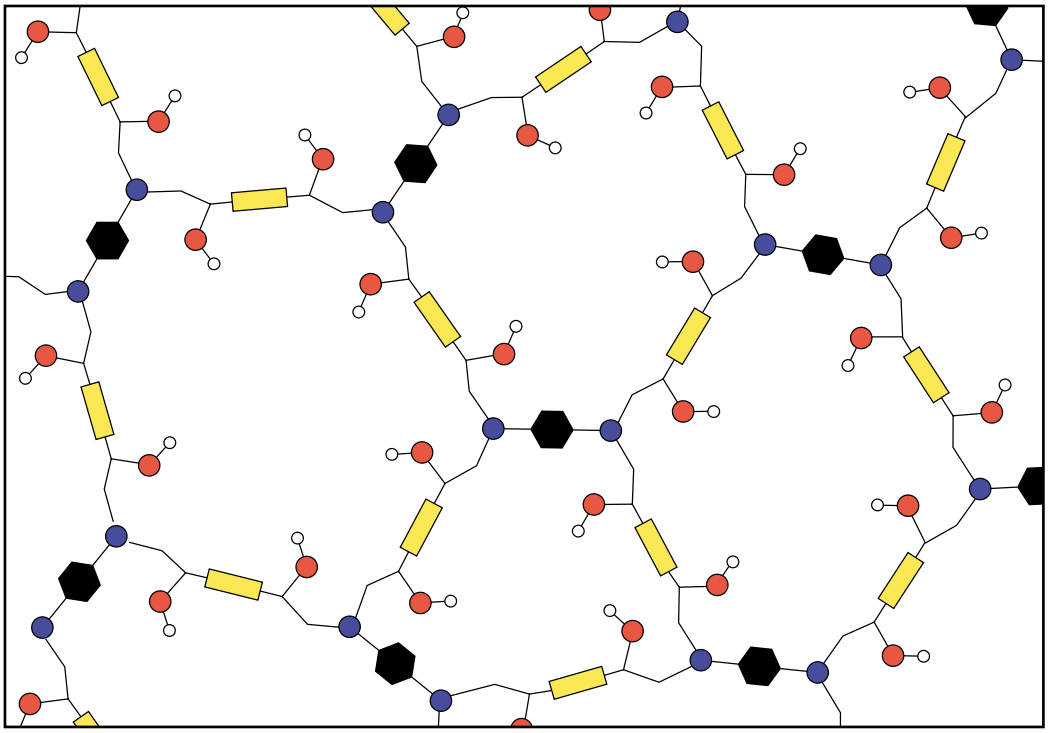
Epoxy Resins

The stoichiometric mixing ratio of an epoxy resin with an amine hardener is calculated as follows:

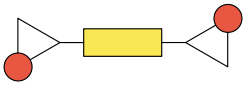
$$\text{parts of curing agent per 100 parts epoxy resin (phr)} = \frac{\text{H-equivalent weight (HEW) of the hardener}}{\text{epoxy-equivalent weight (EEW) of the resin}} \times 100$$

Aliphatic or aromatic amines react with epoxy resins at room temperature, so the processing time is limited. A nearly unlimited shelf life, combined with fast curing at elevated temperatures, are achievable with so-called latent epoxy resin hardeners.

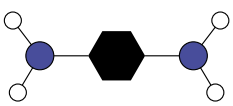
Dicyandiamide, a product of Degussa AG, is the most widely used epoxy resin hardener for curing at elevated temperature. Its applications extend from electrical laminates to composite materials, from structural adhesives to powder coatings.

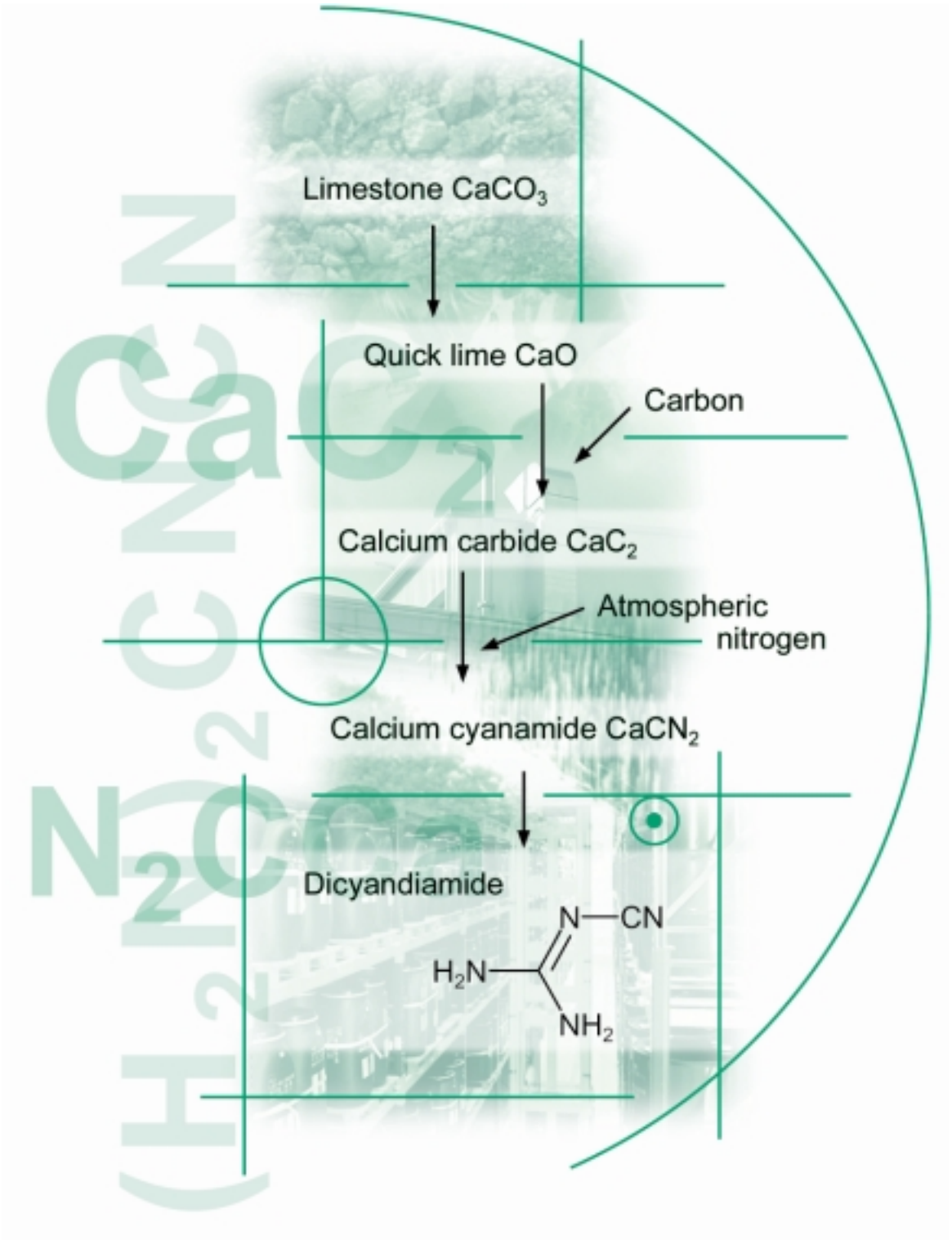


Schematic figure of a polymer network formed by the reaction of an epoxy resin



with a tetrafunctional amine




Limestone $CaCO_3$
Quick lime CaO
Carbon
Calcium carbide CaC_2
Atmospheric nitrogen
Calcium cyanamide $CaCN_2$
Dicyandiamide
N—CN
H_2N
NH_2

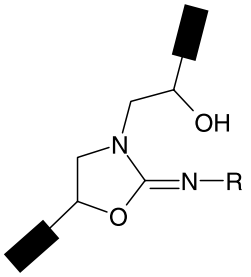
The Dicyandiamide-Epoxy Reaction

At moderate temperatures, dicyandiamide does not react with epoxy resins. This is because of the low basicity and poor solubility in epoxy resins. Dicyandiamide as such reacts very quickly with epoxy resins starting at about 180 °C. The reaction is accelerated autocatalytically by basic intermediates of the hardener reaction.

The reaction mechanism consists of two stages:

a) Addition of the NH groups to the epoxy ring

b) Condensation of OH groups with CN multiple bonds to form heterocyclic systems. 2-Iminooxazolidines (1) and tertiary amines (2) can be considered the main products in the hardened resin [4].



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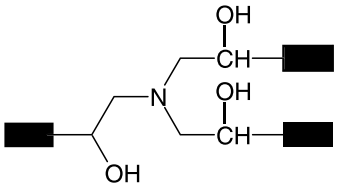
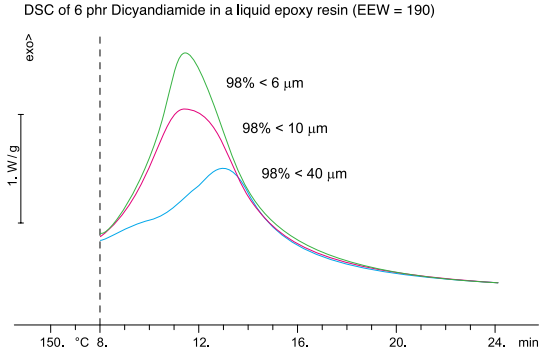


(2)

In contrast to other amine hardeners, the original dicyandiamide molecule degrades into small functional units [5]. Because of the complicated reaction mechanism, the curing reaction does not follow an exact stoichiometry. Depending on hardening conditions, one dicyandiamide molecule reacts with 6–7 epoxy groups. This reaction results in an empirical H-equivalent weight of 12 –14 for dicyandiamide.



The particle size of the dicyandiamide is essential to the achievable properties of the cured resin. Dicyandiamide with large grain size frequently forms inclusions, which can cause the workpiece to fail. Ultramicronized dicyandiamide has the following advantages:

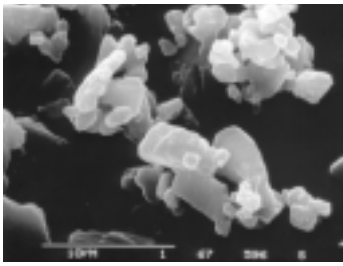
Higher reactivity, no unreacted inclusions with unreacted particles, no mechanical failure, no surface defects on coatings.

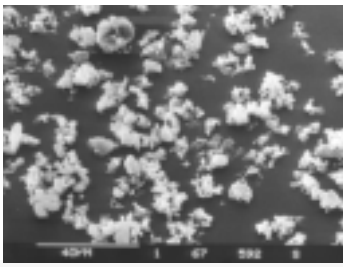
Mixing and Fine Grinding Center

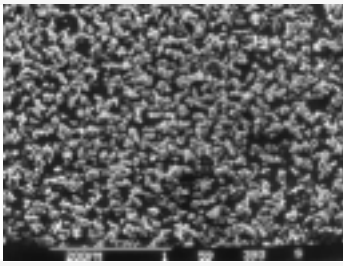
In combination with our dicyandiamide production, high-tech grinding with air jet mills is combined at the Trostberg/Schalchen site in a unique mixing and fine grinding center.

Small grain sizes (down to 6 µm) and narrow grain distribution, as a rule, result in high reactivities of the hardeners and accelerators.

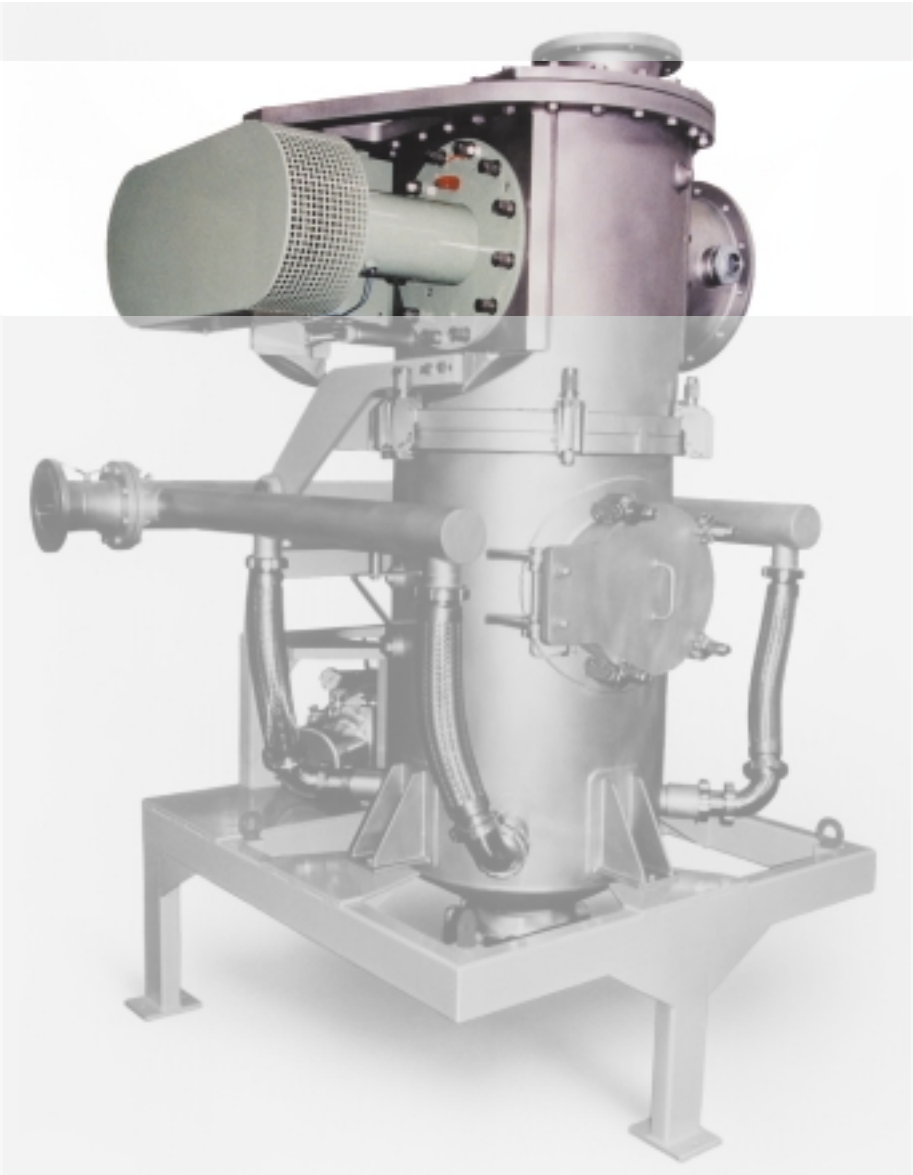
Besides the standard products, this center can also be used for toll production.







Grain sizes, microscopic photographs



air jet mill

image: Hosokawa Alpine

Dyhard® Epoxy Resin Hardeners

Micronized Dicyandiamide:

Dyhard® 100	98% < 40 µm
Dyhard® 100 S	98% < 10 µm
Dyhard® 100 SF	98% < 6 µm

affords the widest range of applications as an epoxy resin hardener. Degussa's high-tech grinding provides for narrow grain size distribution.

Low-turbidity Dicyandiamide for solutions:

Dyhard® T03
Dyhard® G03

special quality for prepregs and electrical laminates with high purity and excellent dissolution properties.

Dyhard® solutions:

Dyhard® L10

for prepregs and electrical laminates, feature low turbidity and reduced effort for resin users.

Dyhard® pastes:

Dyhard® D 50 EP
Dyhard® DF 50 EP

Pastes of micronized dicyandiamide simplify handling and improve dispersibility in liquid epoxy resins as a master batch for composites and adhesives.

Substituted Dicyandiamide:

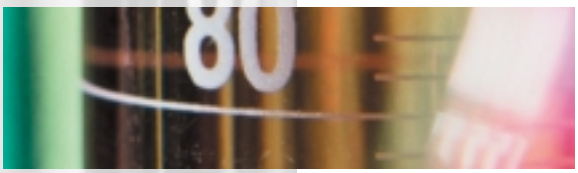
Dyhard® OTB

Yields e.g. high-gloss powder coatings with very good mechanical properties.

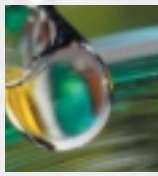
Matt curing agent:

Dyhard® PIN +
Dyhard® CA AB

Dyhard® PIN and Dyhard® CA AB at a mixing ratio of 45% Dyhard® PIN with 55% Dyhard® CA AB results in powder coatings e.g. with low-gloss, high gloss stability and low yellowing.



Dyhard® Accelerators



Why accelerators?

Dicyandiamide, subject to the formulation, offers excellent mechanical and electrical properties and a straightforward processing of the finished resin formulation.

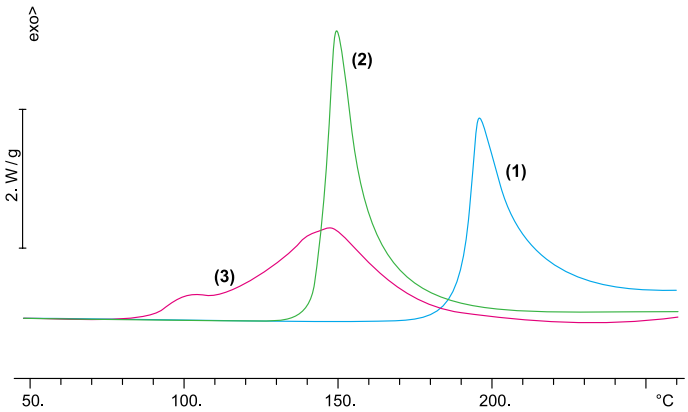
The necessary curing temperatures, however, are too high for many applications. A Dyhard® accelerator reduces the curing temperature and maintains the good properties of the cured resin.

Dyhard® UR types

Blocked accelerators with a high latency, which entail fast curing after the impact of heat.

Dyhard® imidazoles:

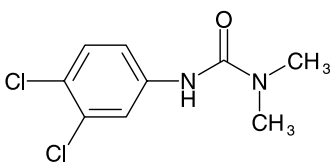
Unblocked accelerators that achieve high curing rates even at low temperatures. They are highly soluble in the epoxy resin but have reduced shelf lives.



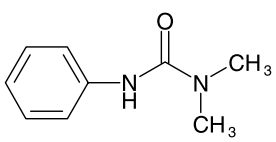
Comparison of the reactivities of epoxy/dicyandiamide formulations

(1) Without accelerator
(2) With blocked accelerator (Dyhard® UR types)
(3) With unblocked accelerator (Dyhard® imidazole)

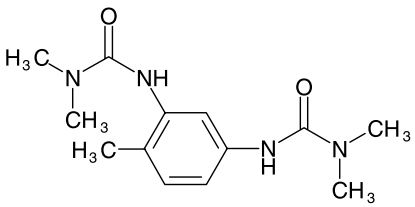
Dyhard® UR Types



Dyhard® UR 200



Dyhard® UR 300



Dyhard® UR 500

Dyhard® Accelerators

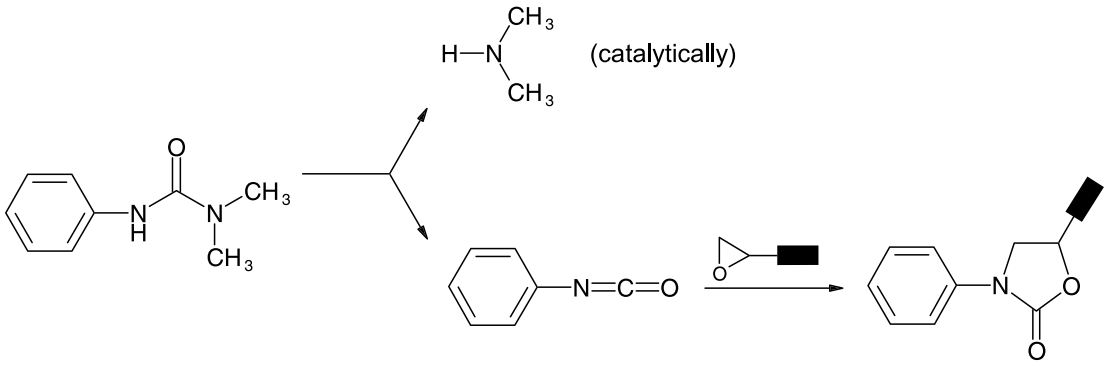
In combination with dicyandiamide, Dyhard® UR types provide for good shelf lives of one-component systems. Above 130 °C, short curing rates are achieved.

Dyhard® UR 500 accelerator is the most reactive UR type. In addition, good TG values are achieved.

Dyhard® UR types decompose under the influence of heat to form isocyanates and catalytically active dimethylamine [6,7,8]. Following activation by heating above the onset temperature, the accelerators lose their latency to form free dimethylamine.

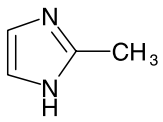
The isocyanates released react with epoxies to form additional linkages via oxazolidinones (3).

The applications for Dyhard® UR types are prepregs for composites and structural adhesives.

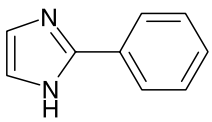


(3)

Dyhard® Imidazoles



Dyhard® MI:



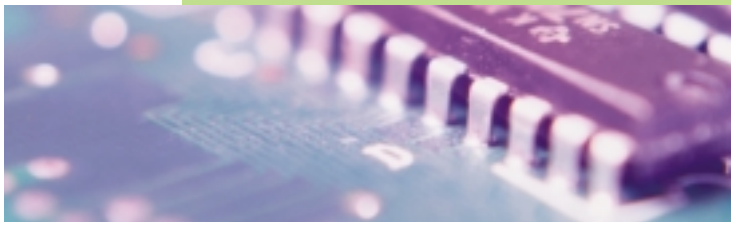
Dyhard® PI:

Dyhard® MIA: 2-Methylimidazole epoxy resin adduct

Because of their unrivaled catalytic properties, imidazoles play a unique role in natural enzymes that catalyze nucleophilic reactions. The action of Dyhard® imidazoles on the dicyandiamide-epoxy reaction is based on the same mechanisms [9].

They afford high reactivities at only 100 °C and provide an appreciable accelerator action with the addition of only 0.1 phr.

The main applications for Dyhard® imidazoles are electrical laminates, adhesives and powder coatings.



Formulation Example for an Impregnating Solution

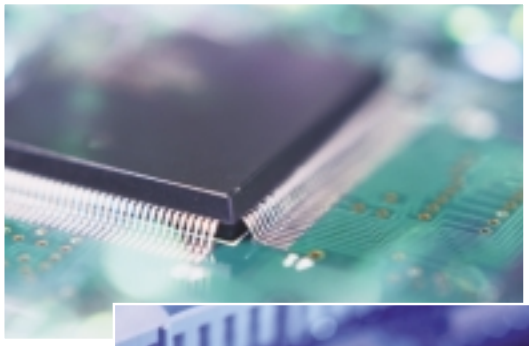
125.0 parts Epikote 1141-B-80 (Resolution)
30.0 parts Dyhard® L 10
10.0 parts methyl glycol
0.1 part Dyhard® MI-C (or Dyhard® PI)

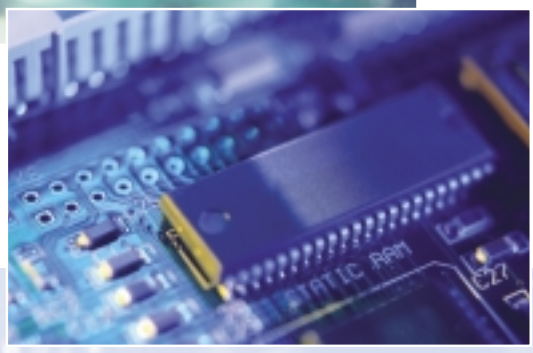
A glass fabric (USType 7628, 200 g/m2, finish Z 6040 by Dow Corning) is impregnated with this solution, then dried and pre-reacted in a hot-air oven. Preferably 8 layers of the prepreg made by this method are compressed in a tiered press at 175 °C to make a FR-4 printed circuit board.

The following printed circuit types are based on the same resin composition: NEMA FR-3, FR-4, CEM-1, CEM-3, DIN ISO EP-CP01, EP-GC02.

Typical requirements to an FR-4 laminate:

Glass transition temperature	135 °C
Water absorption after 24 hr in water at 23 °C	< 0.25%
Solder bath resistance at 260 °C	> 20 sec
Surface resistance	10^{10} ohms
Dielectric constant at 1 MHz	5.4





Dyhard® for printed circuit boards:

Dyhard® T03/G03 hardener
Dyhard® L10 hardener
Dyhard® MI-C, PI accelerator

Composite Materials

Composites are materials greatly demanded in the aeronautics, athletic and automobile industries as replacements for aluminum or wood. An attractive new application is wind vanes for wind power plants.

Formulation Example 1 (Sporting Goods)

100 parts D.E.R. 331 (Dow)
7 parts Dyhard® 100 S
3 parts Dyhard® UR 300

Glass or carbon fiber fabric can be impregnated with this. After pre-reaction in a hot-air oven, the prepreg cures at 140 °C.

Formulation Example 2 (High-Tech Composites)

60	parts Araldite MY 720 (Vantico)
20	parts Epikote 1001 (Resolution)
9	parts Epikote 828 (Resolution)
18.5	parts Dyhard® D 50 EP
4.5	parts Dyhard® UR 500

Unidirectional carbon fiber filaments are impregnated with the preheated resin composition. After compression, the laminates have the following properties:

Resin content:	36%
Tensile strength:	1700 MPa
Tensile modulus:	130 GPa
Interlaminar shear strength:	100 MPa
Compressive strength:	1100 MPa
Modulus of compression:	125 GPa

Dyhard® for Composites:

Dyhard® 100 - 100 SF	**Hardener**
Dyhard® pastes	**Hardener, premixed in liquid resin**
Dyhard® UR types	**Blocked accelerator**
Dyhard® imidazoles	**Unblocked accelerator**
Dyhard® MIA 5	**Accelerator**

Structural Adhesives

A mixture of epoxy resin, hardener, accelerator and fillers is prepared. This mixture is stable in storage if blocked accelerators are used. Curing begins on heating in the range of 100 – 180 °C. Such hot-melt or package adhesives are used, for example, in the automobile industry or in all other uses that require rapid hardening and storage stability.

image: Daimler-Chrysler

Adhesive bonding is better than welding.

1-Component Adhesive for Structural Adhesive Bonding

72.5 parts	Rütapox VE 3356 (Bakelite)
3.4 parts	Dyhard® 100 S
0.2 part	Dyhard® UR 200
4.8 parts	Aerosil R 202 (Degussa)
19.1 parts	Wollastonit (Kemolit) S1 (Osthoff-Petrasch)

Stable for one year of storage at room temperature, hardens at 180 °C.

Impact-Modified 1-Component Adhesive

60 parts	D.E.R. 331 (Dow)
30 parts	D.E.R. 431 (Dow)
13 parts	Dyhard® D 50 EP
2 parts	Dyhard® UR 500
10 parts	Struktol Polydis 3614 (Schill & Seilacher)
4 parts	Aerosil R 805 (Degussa)

Stable in storage for one year, hardens at 150 °C.

Dyhard® for Adhesives:

Dyhard® 100 - 100 SF	**Hardener**
Dyhard® pastes	**Hardener, premixed in liquid resin**
Dyhard® UR types	**Blocked accelerator**
Dyhard® imidazoles	**Unblocked accelerator**

Powder Coatings

Powder coatings consist of solid resin, pigments, fillers, hardeners and accelerators. These substances are mixed, melted in an extruder, and then ground. The powder is sprayed electrostatically, typically on metal surfaces, and hardened at temperatures as low as approximately 160 °C. Powder coatings are environmentally friendly (no organic solvents and less waste) and are increasingly preferred over conventional coatings.

Formulation Example for High-Gloss Coatings

60	parts	Araldite GT 7203 (Vantico)
36	parts	Titanium dioxide 2160 (Kronos Titan)
1.6	parts	Dyhard® 100 S
0.4	part	Dyhard® MI
0.1	part	Perenol F 40 (Henkel)
0.1	part	Benzoin

This mixture obtains a high-gloss coating that provides excellent protection against mechanical and chemical influences. Micronized dicyandiamide also features excellent corrosion protection and optimum surface (ultrafine particles) and is also approved for food contact under FDA, BGA and EU guidelines.

Formulation Example for Matt Hybrid Coatings

100	parts	D.E.R 662 E (Dow)
67.3	parts	Albester 2660 (Eastman)
2.7	parts	Dyhard® PIN
3.3	parts	Dyhard® CA AB
60.6	parts	Titanium dioxide 2160 (Kronos Titan)
29.5	parts	Durcal 5 (Omya)

is extruded at 110 °C (at 200 rpm).
Typical properties of this mixture:

At baking temperature:	10´, 180 °C	10´, 200 °C
Gloss:	18%	20%
Cupping index IE:	6 mm	6 mm
Mandrel bending test:	8 mm	10 mm

The use of Dyhard® PIN/Dyhard® CA AB at a 45 / 55% ratio produces high gloss-stability and low yellowing at different baking temperatures, starting at 170 °C, even in darkly pigmented formulations.

Image: Werndl Büromöbel AG

image: OLIGO Lichttechnik GmbH

Formulation Example for High-Gloss Clear Coatings

100 parts	D.E.R 663 E (Dow)
8 parts	Araldite GT 3032 (Vantico)
6 parts	Dyhard® OTB

is extruded at 95 °C (180 rpm).
Typical properties of this mixture are:

At baking temperature:	15´,160 °C	10´, 180 °C
Gloss (60 °C):	110%	110%
Cupping index IE:	10 mm	10 mm
Mandrel bending test:	< 3 mm	< 3 mm
Ball impact:	> 160 lb/in	> 160 lb/in

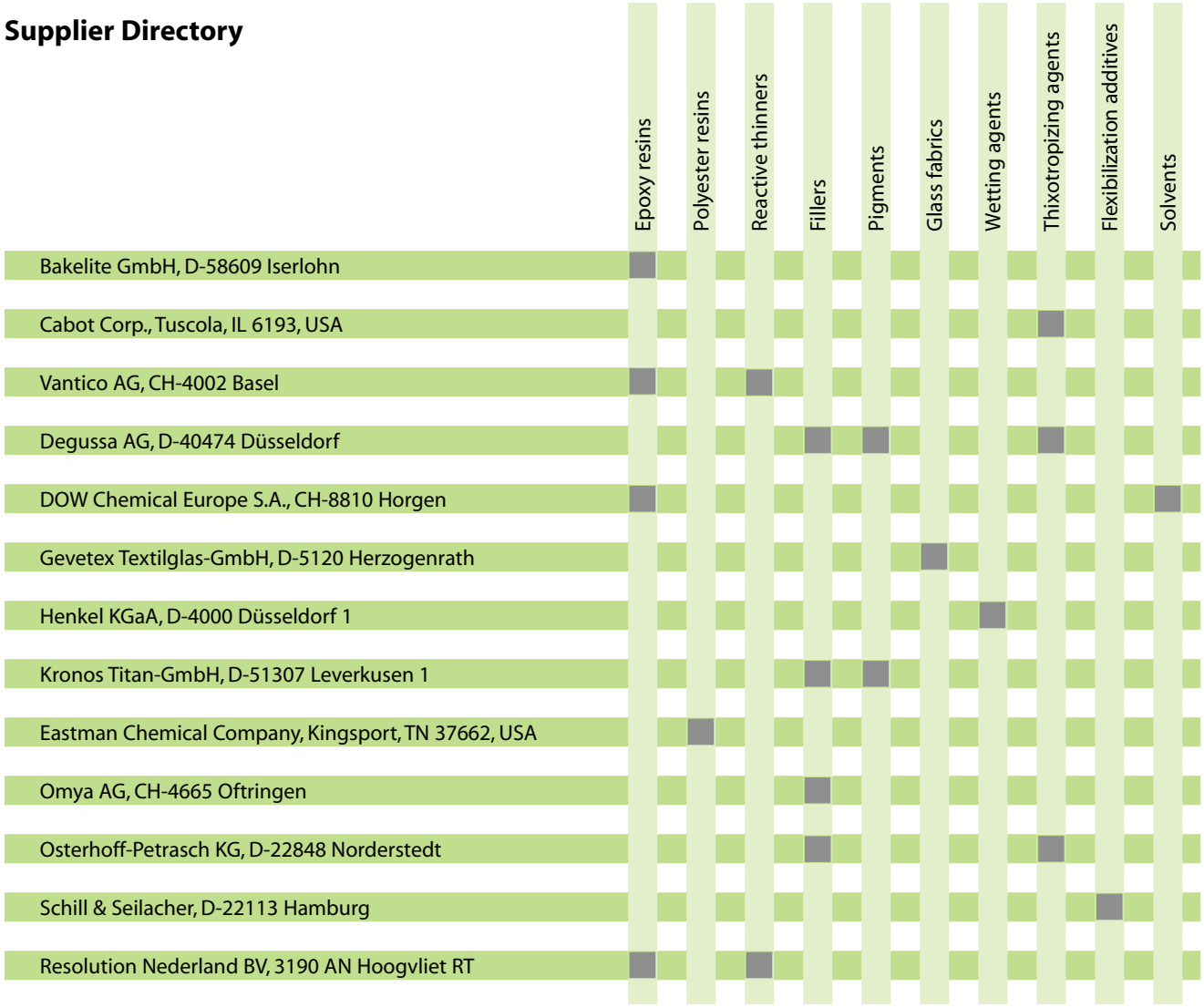
In a high-gloss epoxy system Dyhard OTB gives very good flow properties with best corrosion resistance at low curing temperatures.

Dyhard® for Powder Coating:

Dyhard® 100 - 100 SF	**Hardener**
Dyhard® PIN + CAAB	**Matt curing agent**
Dyhard® OTB	**Hardener**
Dyhard® imidazoles	**Accelerator**
Dyhard® MIA 5	**Accelerator**
Dyhard® UR 300	**Accelerator**

Supplier

Supplier Directory



Comparative Data for Epoxy Resins

	Liquid Resins	Solid Resins	Brominated Epoxy Resins
EEW [g/mol]	188	750	470
Viscosity at 25 °C [Pas]	12	solid	1
Softening Point [°C]	––	100	(solution)
Dicyandiamid dose [phr]	7	1.7	3.0
Bakelite Rütapox	0164		
Vantico Araldite	6010	7004	8011
Dow D.E.R.	311	663	511
Resolution Nederland BV	828	3003	1120

Environmental Safety, Health and Quality

At Degussa AG, the quality of products and services, the protection of the environment, our health, plant and occupational safety are equal goals. An integrated management system used to achieve these goals is recognized outside the company and confirmed through certification programs. Regular internal audits identify and evaluate potentials for improvement . The dedication, creativity and innovative expertise of our employees is the key to the success of this system.

Quality assurance procedures for raw materials, process monitoring and product control provide a quality standard that meets our customers' high standards. This high standard is reinforced by independent modern analytical support.

There is no contradiction between Ecology and Economy. According to our self commitment, we are constantly improving our production processes to reduce any potential environmental impact of our operations and to preserve resources.

Occupational safety is a key criterion for Degussa. We carefully analyse potential safety risks in order to minimise them. Learning from faults and avoiding them, is the most important task.

RESPONSIBLE CARE

ISO 9001 : 2000

ISO 14001, BS 8800

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Contact

Visit us on the Internet at www.dyhard.com or through the Degussa Fine Chemicals home page

www.finechemicals.de

Or call us:

Service Center Western Europe:

Toll-free: +800-31 30 31 30
Dr. Volker Grunwald
Phone: +41-1-27 43-102
Fax: +41-1-27 43-103
E-mail: volker.grunwald@degussa.com

Marketing:

Barbara Huber
Phone: +49 (0) 86 21-86-29 35
Fax: +49 (0) 86 21-86-35 98
E-mail: barbara.huber@degussa.com

Technical Service:

Dr. Sylvia Huber
Phone: +49 (0) 8621-86-2476
Fax: +49 (0) 8621-86-2172
E-mail: sylvia.huber@degussa.com

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Germany
Degussa AG
Fine Chemicals
FI-FC-AG-KD
Dr.-Albert-Frank-Str. 32
D-83308 Trostberg
Phone: +49-8621-86-2935
Fax: +49-8621-86-3598
www.finechemicals.de