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Prepolymeric epoxy resin mixture containing oxazolidinone structures

The invention relates to a process for the preparation of a prepolymeric epoxy resin mixture containing oxazolidinone structures and an apparatus for carrying out this process.

WO 90/15089 discloses that epoxy-terminated polyoxazolidinones (referred to there in simplified form as polyoxazolidones) can be prepared by reacting a polyepoxy compound with a polyisocyanate compound at elevated temperature in the presence of a catalyst. For this purpose, 5 to 30% by weight of the polyisocyanate compound are added in the course of 30 to 90 minutes to a mixture of 70 to 95% by weight of the polyepoxy compound and 0.01 to 2% by weight of the catalyst, and the reaction mixture obtained is heated to a temperature of 110 to 200°C for a period of 5 to 180 minutes. By regulation of various process parameters, the process is carried out in such a way that, in the resulting epoxy-terminated polyoxazolidinone, which is also referred to as isocyanate-modified epoxy resin, 50 to 100% of the original isocyanate groups are converted into oxazolidinone rings and 0 to 50% into isocyanurate rings.

In the known process, bisphenol A and tetrabromobisphenol A are preferably used as the polyepoxy compound, and the polyisocyanate compound is 4,4'-methylenabis(phenyl isocyanate) (MDI) or an isomer thereof, polymeric MDI or

toluylene diisocyanate. An imidazole compound or tetraphenylphosphonium bromide is especially suitable as a catalyst (for the reaction between the polyepoxy compound and the polyisocyanate compound); the catalyst
5 concentration is preferably 0.02 to 1% by weight, in particular 0.02 to 0.1% by weight, based on the total weight of polyepoxy compound and polyisocyanate compound.

For the preparation of the polyoxazolidinones, the catalyst, optionally dissolved in a suitable solvent, is
10 added to the polyepoxy compound, in general at a temperature below the reaction temperature of 110 to 200°C. The temperature is then increased to the reaction temperature and kept there while the polyisocyanate compound is added in a controlled manner, i.e. added dropwise.

15 A similar procedure is adopted in a process disclosed in EP 0 296 450 A1, for the preparation of oligomeric polyepoxides containing oxazolidinone groups (referred to there in simplified form as oxazolidone groups) from
20 bisepoxides and diisocyanates. In this process - at 140 to 180°C in the presence of a phosphonium salt as the catalyst - either bisepoxyethers having OH groups corresponding to an OH number of at least 2 are reacted with aromatic diisocyanates which have two different reactive
25 NCO groups in an amount of at least 1/4 of the weight of the diisocyanate, or bisepoxyesters having OH groups corresponding to an OH number of at least 2 are reacted with aromatic, aliphatic or cycloaliphatic diisocyanates in a ratio of NCO groups to epoxy groups of 1 : 1.4 to
30 1 : 2.5. The catalyst is used in an amount of 0.005 to 1.0% by weight, preferably

0.01 to 0.5% by weight, based on bisepoxide.

5 The essential feature of this process is that the oxazol-
idinone-epoxy resins are obtained only when epoxy resins
containing OH groups are reacted at about 160°C together
with diisocyanates containing NCO groups of different
reactivities - under catalysis by a phosphonium salt. For
the preparation of the polyepoxides, the bisepoxy resin
is heated to 160°C together with the catalyst under
nitrogen. The diisocyanate is then added dropwise to the
10 melt, sufficiently rapidly for a temperature of about
170°C to be maintained. After the addition of all the
diisocyanate, stirring is continued at 160°C until the
calculated epoxide value is reached and reactive NCO is
no longer detectable.

15 Both known processes are described only for batch sizes
on the laboratory scale. It is important that the poly-
isocyanate is added only dropwise to the catalyst-
containing polyepoxide. It is therefore hardly possible
to carry out the stated processes - on an industrial
20 scale - in an economical manner. Furthermore, only
filler-free reaction resin mixtures are used in these
processes.

It is the object of the invention to provide an
industrial process for the preparation of a prepolymeric
25 epoxy resin mixture which contains oxazolidinone struc-
tures, has a long shelf life, is soluble or can be
melted, has latent reactivity and is curable.

This is achieved, according to the invention, if an
insoluble reaction resin powder which is free of iso-
30 cyanate groups

and comprises an epoxy resin mixture containing a reaction accelerator and a filler and containing isocyanurate structures is fed to a continuous reactor and reacted at reaction temperatures up to 200°C, the temperature of the reactor being 140 to 190°C, and if the extrudate is cooled to a temperature of < 50°C with the aid of a cooling apparatus mounted at the outlet nozzle of the reactor.

In the process according to the invention, a suitable continuous reactor is in particular a twin-screw extruder. It is advantageous if, in the extruder, the ratio of the screw length to the outer screw diameter is from 20 to 50, preferably 25 to 40. In addition, the extruder is preferably designed so that the residence time at screw speeds of > 10 min⁻¹ is less than 5 min, preferably less than 3 min, and a minimum axial back-flow results.

The insoluble reaction resin powder which is free of isocyanate groups can be metered into the twin-screw extruder by means of a twin-screw metering apparatus, for example at a mass flow rate of 150 g/min. The extruder contains conveying screw elements (screw diameter, for example, 31.8 mm, screw length 880 mm) and is equipped with five thermostatable barrel zones which are heated, for example, to 160°C. At a screw speed of 90 min⁻¹, the melt residence time is, for example, < 1 min. The extrudate emerging from a slot die is guided along a cooled slide rail and cooled rapidly to temperatures below 50°C, the epoxy resin mixture solidifying to form tape-like continuous strips. These strips are drawn on

a take-off belt under a counter-roller and thus coarsely comminuted. The precomminuted product is milled to the desired particle size in an impact mill. The free-flowing, prepolymeric epoxy resin mixture which is prepared in this manner, has a long shelf life, is soluble or can be melted, has latent reactivity and contains oxazolidinone structures is stored in the absence of moisture.

In the process according to the invention, an insoluble reaction resin powder which is free of isocyanate groups is used. A filler-containing, thermally polymerisable reaction resin mixture of polyepoxy resin and polyisocyanate resin having a molar ratio of epoxy groups to isocyanate groups of > 1 , preferably 1.5 to 4.0, is used for the preparation of this reaction resin powder. The polyepoxy resin is a mixture of di- and polyfunctional epoxy resins, the molar ratio of polyfunctional to difunctional epoxy resin being 0.1 to 1.7 and preferably 0.2 to 0.75, based on the epoxy groups. The reaction resin mixture of polyepoxy resin and polyisocyanate resin is reacted using substituted imidazole as a reaction accelerator, with a content of 0.5 to 2.5%, based on polyepoxy resin, at temperatures up to 180°C.

Whereas in the prior art, as disclosed in particular in the Examples, low catalyst concentrations are used, specifically 0.01 to 0.35% (WO 90/15089) or 0.1% (EP 0 296 450 A1), based in each case on polyepoxide, substantially larger amounts of catalyst are required for the preparation of reactive, curable prepolymeric epoxy resin mixtures. In the process according to the invention, the catalyst concentration is therefore

0.5 to 2.5%, preferably 1.0 to 1.8%, based on the mixture of di- and polyfunctional epoxy resins. These high catalyst concentrations are required so that the prepolymeric epoxy resin mixture having latent reactivity can be
5 cured in an industrially relevant time without subsequent acceleration - which is expensive in the case of filler-containing systems.

For the preparation of the insoluble reaction resin powder which is free of isocyanate groups on the pilot
10 scale, a mixing container, preferably a vertical kneader, is suitable, and a continuous reactor is used for larger amounts. The preparation and processing of the reaction resin mixture in a vertical kneader is carried out in the following manner. The di- and polyfunctional epoxy resins
15 and the polyisocyanate resin are introduced into the vertical kneader which is equipped with a thermostatable and evacuable kneading trough and with kneading blades and permits continuous temperature measurement in the reaction resin mixture, heated to temperatures of up to
20 100°C, mixed while stirring and devolatilised. The filler and optionally further additives are introduced in portions into the heated reaction resin mixture, and devolatilisation is carried out - with further stirring - at a temperature of up to 100°C under reduced pressure
25 for at least 1 h. The reaction accelerator is then mixed in. The temperature of the mixing container is then adjusted to 160 to 180°C. The conversion of the reaction resin mixture to the reaction resin powder takes place, as a rule, at reaction temperatures of 130°C or higher
30 within a few minutes, a free-flowing product being formed in the mixing container as a result of the continuous stirring. To terminate the reaction, the temperature of the mixing container is rapidly reduced with the aid of a cooling thermostat

and the reaction resin powder is brought to temperatures of less than 50°C while stirring. The intended conversion of the epoxy groups at the time of termination of the reaction is determined in preliminary experiments. It is
5 shown by IR spectroscopy that no further isocyanate groups are present in the reaction resin powder. The free-flowing, insoluble reaction resin powder obtained in this manner and having a long shelf life can be stored for a relatively long time in the absence of moisture,
10 depending on requirements.

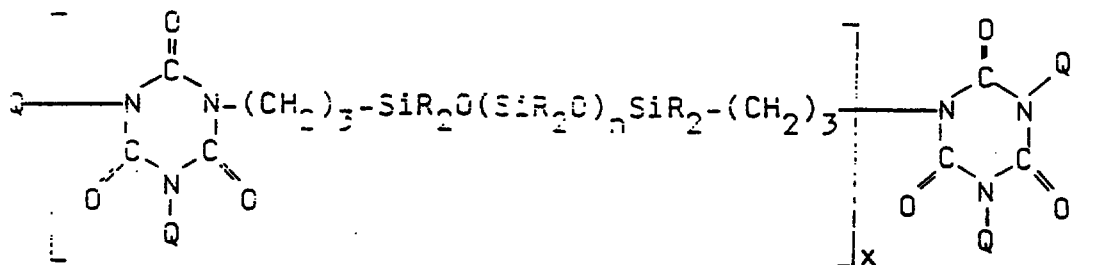
When a continuous reactor is used for the preparation of the insoluble reaction resin powder which is free of isocyanate groups, the preparation of the reaction resin mixture and the feeding thereof to the reactor can be
15 carried out in various ways. In one case - for the preparation of a resin component - the di- and poly-functional epoxy resins and the polyisocyanate resin and the filler are devolatilised in a thermostatable and evacuable mixing container while stirring at temperatures
20 up to 100°C. In a second mixing container - for the preparation of an accelerator component - the reaction accelerator is dissolved or dispersed in one of the resin components intended for the formulation or in a portion thereof, with devolatilisation. The two components are
25 then fed to a static mixing tube, and the reaction resin mixture emerging from the mixing tube is metered into the reactor.

In another case, the resin component is prepared as in the first case. For the preparation of the accelerator component, the reaction accelerator is thoroughly mixed
30 with a portion of the filler intended for the formulation. The two components are then metered into a twin-screw extruder, for example by means of

a peristaltic pump or a twin-screw powder metering apparatus. In contrast to the twin-screw extruder already described, the extruder used for the preparation of the insoluble reaction resin powder contains both conveying screw elements and kneading elements and is equipped with a larger number of thermostatable barrel zones.

The reaction of the resin component and of the accelerator component to give the insoluble reaction resin powder which is free of isocyanate groups is preferably carried out at lower temperatures than the reaction of the reaction resin powder to give a prepolymeric epoxy resin mixture. The free-flowing reaction resin powder which has a long shelf life can be metered into the continuous reactor in a simple manner without expensive metering systems. Thus, for example, free-flowing mixtures of the reaction resin powders having different compositions or mixtures with fillers and/or additives can be metered into the continuous reactor and processed for product optimisation without great expense.

As already mentioned, a polyepoxy resin mixture, i.e. a mixture of di- and polyfunctional epoxy resins, is used for the preparation of the insoluble reaction resin powder. Suitable epoxy resins are preferably bisphenol A and bisphenol F epoxy resins and phenol novolak and cresol novolak epoxy resins or silicone epoxy resins, triglycidyl isocyanurate, tetraglycidyl diamine diphenylmethane and polyglycidyl phosphorus resins. In particular, compounds having the following structure serve as silicone epoxy resins:



where the following is applicable:

n is an integer of 0 to 25,

x is an integer of 0 to 3,

R = alkyl or aryl and

5 Q = $-(CH_2)_3SiR_2O(SiR_2O)_nSiR_2R'$,

in which n and R have the abovementioned meaning and R' is an epoxy functional radical having 6 carbon atoms.

10 The content of silicone epoxy resin is up to 20%, preferably 1 to 7%, based in each case on the filler-free reaction resin mixture comprising polyepoxy resin and polyisocyanate resin.

15 Isomer mixtures of diisocyanatodiphenylmethane are preferably used as the polyisocyanate resin. However, for example, isomer mixtures of toluylene diisocyanate and prepolymers of isomer mixtures of diisocyanatodiphenylmethane are also suitable. Mixtures of the stated polyisocyanate resins can also be used.

20 Substituted imidazoles are used as reaction accelerators in the process according to the invention. 2-Ethyl-4-methylimidazole, 2-phenylimidazole and 1-cyanoethyl-2-phenylimidazole are preferably used. Further suitable reaction accelerators are, for example, 1,2-dimethylimidazole, 1-cyanoethyl-2-methylimidazole,

2-isopropylimidazole and 1-benzyl-2-phenylimidazole. The content of reaction accelerator is 0.5 to 2.5%, preferably 1.0 to 1.8%, based on polyepoxy resin, i.e. on the mixture of di- and polyfunctional epoxy resins.

5 Suitable fillers are in particular mineral fillers, such as quartz in the form of splinters and/or spherical particles (different particle size distribution). Ceramic fillers, such as alumina, and mixtures of ceramic fillers and mineral fillers may also be used. Fibrous fillers,
10 such as short glass fibres, are also suitable.

In the process according to the invention, the composition of the reaction resin mixture comprising polyepoxy resin and polyisocyanate resin differs radically from that of reaction mixtures used in the prior art. For the
15 preparation of the reaction resin mixture, mixtures of di- and polyfunctional epoxy resins are in fact used, i.e. mixtures of epoxy resins having different chemical compositions and different functionalities. However, such mixtures are not known from the prior art. In addition,
20 neither the particularly suitable reaction accelerator 1-cyanoethyl-2-phenylimidazole nor the silicone epoxy resins of the stated type - which are important for the processing properties - and tetraglycidyl-diaminodiphenylmethane - which is particularly suitable for increasing
25 the glass transition temperature - are mentioned there.

The preparation of free-flowing reaction resin powders which have a long shelf life, are free of isocyanate groups and contain isocyanurate structures from a mixture of di- and polyfunctional

epoxy resins with polyisocyanate resin in a molar ratio of epoxy groups to isocyanate groups of > 1 using substituted imidazole as a reaction accelerator has not been described to date. The preparation of resin mixtures containing accelerator and filler from epoxy and isocyanate resins which are solid at room temperature and an imidazole compound is known, the components being mixed by kneading at 80°C (cf.: Japanese Published Application 50-059499 and Japanese Published Application 51-128400). These accelerator-containing resin mixtures are cured at temperatures up to 180°C with shaping. In contrast to the process according to the invention, it is not insoluble reaction resin powders free of isocyanate groups which are prepared but resin mixtures which can be melted and which can be processed with shaping.

For a person skilled in the art, it could not be foreseen that a prepolymeric epoxy resin mixture which is soluble or can be melted is preparable from the insoluble reaction resin powder which is free of isocyanate groups (chemically crosslinked) - in the process according to the invention - by reaction extrusion. Surprisingly, polyfunctional epoxy resins contained in the reaction resin powder, such as the stated silicone epoxy resins and tetraglycidyl-diaminodiphenylmethane, and the use of high accelerator concentrations and temperatures up to 200°C do not lead here to further curing of the reaction resin powder but instead to a curable epoxy resin mixture which has a long shelf life, is soluble or can be melted and can be cured without subsequent acceleration - which is expensive in the case of filler-containing reaction resins.

The invention is to be illustrated in detail with reference to Examples.

Example 1

Preparation of an insoluble reaction resin powder which is free of isocyanate groups

1,530 g of bisphenol A epoxy resin (epoxide value:
5 5.78 mol/kg), 99 g of a silicone epoxide (epoxide value:
1.9 mol/kg), prepared according to Example 9 of European
Offenlegungsschrift 0,399,199, 495 g of tetraglycidyl-
diaminodiphenylmethane (epoxide value: 8.2 mol/kg) and
360 g of an isomer mixture of diisocyanatodiphenylmethane
10 (isocyanate value: 7.9 mol/kg) are introduced into a
vertical kneader, then heated to 80°C and mixed with
stirring. Thereafter, 4,347 g of spherical quartz,
1,863 g of quartz splinters and 90 g of carbon black are
added in portions to the mixture while stirring; devolat-
15 ilisation is then carried out for 1 h at 80°C while
stirring. 33.3 g of 1-cyanoethyl-2-phenylimidazole are
metered into the reaction resin mixture, and devolat-
ilisation is then carried out for 10 min while stirring.
Thereafter, the temperature of the mixing container is
20 adjusted to 160°C and the reaction resin mixture is
heated while stirring. The reaction to give the reaction
resin powder is initiated at about 130°C; the course of
the reaction is monitored continuously by temperature
measurement. The reaction is terminated 1 min after the
25 solidification of the reaction resin mixture, by cooling
the mixing container by means of a cooling thermostat.
The temperature of the reaction resin is then reduced to
less than 50°C with further stirring. As a result of the
continuous stirring, the insoluble reaction resin is
30 obtained as a free-flowing powder having a long shelf
life (epoxide value: 1.28 mol/kg). It is shown by IR
spectroscopy that no further isocyanate groups are
present in this product.

Example 2

Preparation of a prepolymeric epoxy resin mixture containing oxazolidinone structures

The insoluble reaction resin powder prepared according to Example 1 and free of isocyanate groups is fed with the aid of a powder metering apparatus at a continuous mass flow rate of 30 g/min to a twin-screw extruder having screws rotating in the same direction (screw length: 880 mm, outer screw diameter: 31.8 mm); the screws of the extruder consist exclusively of conveying elements. The five barrel zones of the extruder are adjusted to 160°C; the following temperatures are produced in the individual barrel zones: zone 1: 152°C, zone 2: 158°C, zone 3: 160°C, zone 4: 160°C, zone 5: 155°C. The screw speed is 90 min⁻¹, resulting in a melt residence time in the extruder of 1.0 min. The extrudate is discharged through a double slot die (cross-section: 2 mm x 20 mm each), cooled to a temperature of less than 50°C by means of a cooled slide rail and coarsely comminuted on a connected elastic take-off belt by means of a counter-roller. The precomminuted extrudate is milled to the desired particle size by means of an impact mill. The resulting free-flowing, curable prepolymeric epoxy resin mixture having latent reactivity (epoxide value: 0.86 mol/kg; melting range: 75 to 95°C) is stored at room temperature in the absence of moisture.

Example 3

Preparation of an insoluble reaction resin powder which is free of isocyanate groups

825.2 g of bisphenol A epoxy resin (epoxide value:
5 5.78 mol/kg), 50.1 g of a silicone epoxide (epoxide
value: 1.9 mol/kg), prepared according to Example 9 of
European Offenlegungsschrift 0,399,199, 262.1 g of tetra-
glycidyl-diaminodiphenylmethane (epoxide value: 8.2 mol/
kg) and 286.4 g of an isomer mixture of diisocyanato-
10 diphenylmethane (isocyanate value: 7.9 mol/kg) are
introduced into a vertical kneader, then heated to 85°C
and mixed with stirring. Thereafter, 7,560 g of alumina
(particle size < 150 μ m) are added in portions to the
mixture while stirring; devolatilisation is then carried
15 out for 1 h at 85°C. 16.2 g of 2-phenylimidazole are
metered into the reaction resin mixture, and devolatil-
isation is then carried out for 10 min while stirring.
Thereafter, the reaction resin mixture is further treated
in a corresponding manner as in Example 1. An insoluble
20 reaction resin which is free of isocyanate groups is
obtained in the form of a free-flowing powder (epoxide
value: 0.7 mol/kg).

Example 4

Preparation of a prepolymeric epoxy resin mixture con-
25 taining oxazolidinone structures

The insoluble reaction resin powder prepared according to
Example 3 and free of isocyanate groups is fed to a twin-
screw extruder according to Example 2 with the aid of a
powder metering apparatus at a continuous mass flow rate
30 of 60 g/min. The five barrel zones of the extruder

are adjusted to 165°C; the following temperatures are produced in the individual barrel zones: zone 1: 155°C, zone 2: 162°C, zone 3: 165°C, zone 4: 165°C, zone 5: 159°C. The screw speed is 95 min⁻¹, resulting in a melt residence time in the extruder of 0.9 min. In the further procedure according to Example 2, a free-flowing, curable prepolymeric epoxy resin mixture having latent reactivity is obtained (epoxide value: 0.49 mol/kg; melting range: 75 to 95°C) and is stored at room temperature in the absence of moisture.

Example 5

Preparation of an insoluble reaction resin powder which is free of isocyanate groups

For the preparation of a resin component, 2,550 g of bisphenol A epoxy resin (epoxide value: 5.78 mol/kg), 155 g of a silicone epoxide (epoxide value: 1.9 mol/kg), prepared according to Example 9 of European Offenlegungsschrift 0,399,199, 810 g of tetraglycidylldiaminodiphenylmethane (epoxide value: 8.2 mol/kg) and 885 g of an isomer mixture of diisocyanatodiphenylmethane (isocyanate value: 7.9 mol/kg) are introduced into a thermostatable and evacuable mixing container (effective capacity: 20 l), then heated to 60°C and mixed with stirring. Thereafter, 6,195 g of spherical quartz, 2,655 g of quartz splinters and 135 g of carbon black are added in portions to the mixture while stirring; devolatilisation is then carried out for 1 h at 60°C while stirring. For the preparation of an accelerator component, 1,050 g of spherical quartz, 450 g of quartz splinters, 15 g of carbon black and 55.5 g of 1-cyanoethyl-2-phenylimidazole are homogeneously mixed. The resin component is metered into a twin-screw extruder by means of a peristaltic pump at a continuous

mass flow rate of 42 g/min, and the accelerator component by means of a twin-screw metering apparatus at a continuous mass flow rate of 5 g/min. The twin-screw extruder is extended by a mixing zone before the process zone and
5 by a discharge zone after the process zone; the extrudate is discharged from the extruder without the use of an extrusion die. The screw length is 1,232 mm and the outer screw diameter 31.8 mm. The screws of the extruder have the following structure: the feed zone contains conveying
10 screw elements, and kneading elements are provided in the subsequent mixing zone, conveying screw elements in the process zone and once again kneading elements at the end of the screws, in order to comminute the extrudate to a uniform particle size and discharge it from the open
15 extruder. The seven barrel zones of the extruder are adjusted to the following temperature: zone 1 (mixing zone): 62°C, zone 2: 110°C, zones 3 to 7: 150°C. The screw speed is 80 min⁻¹, resulting in a melt residence time in the twin-screw extruder of 1.3 min. The extrudate
20 is cooled to 40°C by a cooled slide rail. The resulting insoluble reaction resin powder which is free of isocyanate groups (epoxide value: 1.38 mol/kg) is stored at room temperature.

Example 6

25 Preparation of a prepolymeric epoxy resin mixture containing oxazolidinone structures

The insoluble reaction resin powder prepared according to Example 5 and free of isocyanate groups is fed to a twin-screw extruder corresponding to Example 2 with the aid of
30 a powder metering apparatus at a continuous mass flow rate of

150 g/min. The five barrel zones of the extruder are adjusted to 170°C; the following temperatures are produced in the individual barrel zones: zone 1: 162°C, zone 2: 166°C, zone 3: 170°C; zone 4: 170°C, zone 5: 163°C.

- 5 The screw speed is 100 min⁻¹, resulting in a melt residence time in the extruder of 0.8 min. In the further procedure according to Example 2, a free-flowing, curable prepolymeric epoxy resin mixture having latent reactivity is obtained (epoxide value: 0.84 mol/kg; melting range: 10 75 to 95°C) and is stored at room temperature in the absence of moisture.



Patent Claims

1. Process for the preparation of a prepolymeric epoxy resin mixture containing oxazolidinone structures, characterised in that an insoluble reaction resin powder
5 which is free of isocyanate groups and comprising an epoxy resin mixture containing a reaction accelerator and filler and containing isocyanurate structures is fed to a continuous reactor and reacted at reaction temperatures up to 200°C, the temperature of the reactor being 140 to
10 190°C, and that the extrudate is cooled to a temperature of < 50°C with the aid of a cooling apparatus mounted at the outlet nozzle of the reactor.
2. Process according to Claim 1, characterised in that the reaction resin powder is prepared from a filler-
15 containing, thermally polymerisable reaction resin mixture of polyepoxy resin, comprising a mixture of di- and polyfunctional epoxy resins, and polyisocyanate resin having a molar ratio of epoxy groups to isocyanate groups of > 1 at temperatures of up to 180°C - using substituted
20 imidazole as a reaction accelerator, with a content of 0.5 to 2.5%, based on polyepoxy resin.
3. Process according to Claim 2, characterised in that the reaction resin powder is prepared in a kneader or a continuous reactor.
- 25 4. Process according to any of Claims 1 to 3, characterised in that



a bisphenol A or bisphenol F epoxy resin, a phenol novolak or cresol novolak epoxy resin, a silicone epoxy resin, triglycidyl isocyanurate, tetraglycidyl diamino-diphenylmethane or a polyglycidylphosphorus resin is used
5 as the epoxy resin.

5. Process according to one or more of Claims 1 to 4, characterised in that, in the epoxy resin mixture, the molar ratio of polyfunctional to difunctional epoxy resin is 0.2 to 0.75, based on the epoxy groups.

10 6. Process according to one or more of Claims 1 to 5, characterised in that an isomer mixture of diisocyanatodiphenylmethane or of toluylene diisocyanate or a prepolymer of an isomer mixture of diisocyanatodiphenylmethane is used as the polyisocyanate resin.

15 7. Process according to one or more of Claims 1 to 6, characterised in that 2-ethyl-4-methylimidazole, 2-phenylimidazole or 1-cyanoethyl-2-phenylimidazole is used as the reaction accelerator.

20 8. Process according to one or more of Claims 1 to 7, characterised in that mineral fillers, such as quartz, and/or ceramic fillers, such as alumina, are used.

9. Apparatus for carrying out the process according to one or more of Claims 1 to 8, characterised in that the continuous



reactor is a twin-screw extruder, the ratio of the screw length to the outer screw diameter being 20 to 50, preferably 25 to 40.

10. Apparatus according to Claim 9, characterised in
5 that the shafts of the reactor comprise conveying screw elements or conveying screw and kneading elements and the residence time is < 5 min, preferably < 3 min, at speeds of $> 10 \text{ min}^{-1}$ and minimum axial back-flow.