

GR 92 P 3381 P

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Process for the preparation of a flame-retardant epoxy resin moulding material

The invention relates to a process for the preparation of a flame-retardant, free-flowing, latently
5 reactive phenolically curable epoxy resin moulding material for the coating of components in electronics.

In the electronics industry, filler-containing moulding materials based on epoxy resins are used for coating active and passive components. Examples of such
10 applications are the coating of capacitors, diodes, transistors, power semiconductors, optocouplers, memory chips and microprocessors. Epoxy resin moulding materials which are suitable for this purpose must meet high requirements with regard to the processing and moulding
15 material properties. This relates in particular to the purity of the moulding materials and the rheological behaviour and the curing properties during processing as transfer moulding materials by the transfer moulding process, and also the mechanical and thermal properties
20 of the epoxy resin moulding materials and the stable long-term protection of the components against aggressive environmental influences. In addition, the epoxy resin moulding materials must meet the high requirements in electronics with regard to flame-resistant behaviour and
25 - in the conventional international flammability test according to UL 94 - must achieve the classification V-0 at a layer thickness of ≤ 1.6 mm.

Curing of epoxy resin moulding materials can be carried out using chemically different curing components,
30 for example using carboxylic anhydrides, amines or phenols. However, phenolically curable epoxy resin transfer moulding materials highly filled with silanised quartz powder are usually used for coating electronic components by the transfer moulding process.

35 Phenolically curable epoxy resin transfer moulding materials contain, as a rule, 20 to 30% of organic substances and 70 to 80% of inorganic substances. The chemical basis of the resin components consists in

most cases of cresol novolac epoxy resins. Phenol novolacs are predominantly used for curing the epoxy resins; the reaction is accelerated, for example, with triphenylphosphine, phenylphosphonium borate and 2-ethyl-4-methylimidazole. To improve the low-stress behaviour, silicone-modified epoxy resin components are used. The moulding materials are rendered flame-retardant with aromatic bromine compounds, in particular with tetrabromobisphenol A epoxy resins, which are incorporated chemically into the epoxy resin moulding material during curing. In addition, antimony trioxide serves as a synergistic agent and increases the efficiency of the brominated flameproofing agent. The flame-retardant properties of the epoxy resin moulding materials are further supported by a high content of silanised quartz fillers; both splinter-like fillers and mixtures of splinter-like and spherical fillers are used. Recently, synthetically produced α -radiation-free quartz fillers have been used to avoid so-called soft errors in highly integrated circuits. The high content of silanised quartz filler also serves for improving the mechanical and thermal properties of the epoxy resin moulding materials, in particular for adjusting the coefficient of expansion.

The moulding materials also contain small amounts of additives, in particular carbon black, and processing assistants, such as stearates and waxes.

For the preparation of the phenolically curable epoxy resin transfer moulding materials, the resin and curing components are as a rule converted to a prereacted state (B stage) at temperatures up to about 120°C, in particular by kneading in a roll mill or by extrusion, for example by means of a screw-type kneader, and are powdered. For processing the transfer moulding materials by the transfer moulding process, the moulding material powder is generally pelleted, and if necessary the pellets are preheated to 80 to 90°C. Coating of the components is effected in general at mould temperatures

of 170 to 190°C and at a pressure of 70 to 200 bar, the moulding material being cured in the mould in general for 60 to 120 s. The components are then removed from the mould and are post-cured, as a rule at temperatures of 170 to 190°C.

The phenolically curable epoxy resin moulding materials which have been rendered flame-retardant with bromine-containing flameproofing agents and antimony trioxide and have outstanding flame-retardant properties have proved successful in the electronic industry. Owing to the poor environmental compatibility of the brominated aromatic compounds, however, the substitution of such epoxy resin moulding materials is being increasingly required. The reasons for this are that the stated compounds release highly corrosive brominated gases in the event of faults, i.e. in the event of fire or smouldering, and form poorly biodegradable brominated decomposition products which are potentially highly toxicologically and ecologically dangerous. In addition, epoxy resin moulding materials which contain brominated flameproofing agents are unsuitable for recycling if it is intended to avoid a further spread of hazardous products. Moreover, the disposal of such epoxy resin moulding materials by burning can be carried out in future only as special waste by technically complicated and economically unprofitable incineration processes, owing to the increasing requirements for air pollution control. A disadvantage of the use of antimony trioxide is the fact that this compound is on the list of carcinogenic hazardous materials. Although the danger is negligible in the case of permanently bound materials, antimony trioxide released - in the form of inhalable dust - during a fire or smouldering or in recycling processes constitutes a high risk.

It is the object of the invention to provide a method for the preparation of halogen-free moulding materials based on epoxy resins, which meet the high requirements in electronics with regard to flame-

retardant behaviour and at the same time meet the high requirements with regard to the processing properties and the moulding materials properties. In addition, these moulding materials should have environmentally compatible properties, should be suitable for recycling and should be capable of being disposed of by environment-friendly incineration processes with energy recovery.

This is achieved according to the invention when a prepolymeric epoxy resin mixture free of isocyanate groups and having latent reactivity is prepared in powder form from a filler-containing, thermally polymerisable reaction resin mixture of polyepoxy resin, comprising a mixture of di- and polyfunctional epoxy resins, and polyisocyanate resin in a molar ratio of epoxy groups to isocyanate groups of > 1 - using substituted imidazole as a reaction accelerator in a concentration of 0.5 to 2.5%, based on polyepoxy resin - at reaction temperatures up to 200°C and if the prepolymeric epoxy resin mixture is mixed with a pulverulent, filler-containing phenol resin mixture in a molar ratio of epoxy groups to phenolic hydroxyl groups of 1 : 0.4 to 1 : 1.1, optionally with the addition of additives.

In the process according to the invention, the prepolymeric epoxy resin mixture can be prepared in various ways. In a first variant, polyepoxy resin, i.e. di- and polyfunctional epoxy resins, and polyisocyanate resin and optionally additives are heated to temperatures of up to 100°C in a thermostatable and evacuable mixing container (as a preparation and reaction vessel) which is equipped, for example, with a high-speed stirrer (with duplex kneading blades) and permits continuous temperature measurement, and are mixed with stirring and devolatilised. Filler and optionally further additives are introduced in portions into the reaction resin mixture, and devolatilisation is then carried out with stirring - at temperatures of up to 100°C - for at least 1 h. The reaction accelerator is then metered in and the reaction resin mixture is devolatilised while stirring.

The temperature of the mixing container is then adjusted to 160 to 180°C. The reaction to give the prepolymeric epoxy resin mixture is initiated, as a rule, at a temperature of 130°C in the resin mixture. Depending on
5 the chemical composition of the polyepoxy resin and polyisocyanate resin and on the molar ratio and depending on the type and concentration of accelerator, the reaction temperature may increase to 200°C for a short time.

10 The temperature- and time-monitored reaction is terminated when the prepolymeric epoxy resin mixture is present. Termination is effected by cooling the prepolymeric epoxy resin mixture to temperatures below 50°C. The intended conversion of the epoxy groups at the time
15 of termination of the reaction is established in preliminary experiments and depends on the molar ratio of the epoxy and isocyanate groups used. Important criteria for the termination of the polymerisation reaction are the melting range and the viscosity of the prepolymeric
20 epoxy resin mixture. It is shown by IR spectroscopy that no further isocyanate groups are present in the prepolymeric epoxy resin mixture.

The prepolymeric epoxy resin mixture which is obtained in the reaction described above, is free of
25 isocyanate groups and has latent reactivity is furthermore powdered, which can be effected by milling at room temperature with an impact mill. The pulverulent epoxy resin mixture is then stored in the absence of moisture.

In a second variant - for the preparation of a
30 resin component - polyepoxy resin and polyisocyanate resin are mixed at temperatures of up to 100°C while stirring in a thermostatable and evacuable mixing container which is equipped, for example, with a helical stirrer and permits continuous temperature measurement in
35 the resin mixture. Filler and optionally additives are mixed into this resin mixture, and devolatilisation is then carried out with stirring at a temperature of up to 100°C for at least 1 h. 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 then fed to a static mixing tube by means of metering pumps, for example by means of a heatable peristaltic pump or a gear pump, and the reaction resin mixture emerging from the mixing tube is metered into a continuous reactor.

10 A suitable reactor is preferably a twin-screw extruder. It is advantageous if, in the extruder, the ratio of the screw length to the outer screw diameter is 20 to 50 and preferably 25 to 40. In addition, the extruder is preferably designed so that the melt residence time at screw speeds of $> 10 \text{ min}^{-1}$ is less than 5 min, preferably less than 3 min, and minimum axial back-flow results.

The extruder to which amounts of resin of 20 to 200 g/min are continuously fed 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 to 180°C; the screw speed is 15 to 30 min^{-1} . This gives a residence time in the reactor of less than 3 min for the conversion of the reaction resin mixture into the prepolymeric epoxy resin mixture. The extrudate emerging from the slot die is guided along a cooled slide rail and rapidly cooled to temperatures below 50°C, the epoxy resin mixture solidifying to tape-like continuous strips.

25 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 and has latent reactivity is stored in the absence of moisture.

In a third variant, the preparation of the resin component is carried out as in the second case. For the

preparation of the accelerator component, the reaction accelerator is thoroughly mixed with a portion of the filler intended for the formulation. The two components are then metered into a twin-screw extruder, for example
5 by means of a peristaltic pump or a twin-screw powder metering apparatus. In contrast to the second variant, here the screws in the mixing zone of the extruder, which is adjacent to the feed zone, are provided with conveying kneading elements; the temperature in the mixing zone is
10 up to 100°C. The further structure of the extruder and the processing conditions correspond substantially to variant 2.

In a fourth variant, a free-flowing, insoluble reaction resin powder which has a long shelf life and is
15 free of isocyanate groups is first prepared. This reaction resin powder is then converted into the prepolymeric epoxy resin mixture with the aid of a continuous reactor. For the preparation of the reaction resin powder, an accelerator-containing reaction resin mixture is prepared
20 in a mixing container as in the first case. The temperature of the mixing container is then adjusted to 160 to 180°C. The conversion of the reaction resin mixture into the insoluble reaction resin powder free of isocyanate groups is carried out, as a rule, at reaction tempera-
25 tures of 130°C or higher, in the course of a few minutes, a free-flowing product being formed in the mixing container as a result of stirring. To terminate the reaction, the temperature of the mixing container is rapidly reduced by means of a cooling thermostat, and the
30 reaction resin powder is brought to temperatures of 50°C while stirring. The intended conversion of the epoxy groups at the time of termination of the reaction was determined in preliminary experiments. It is shown by IR spectroscopy that no further isocyanate groups are
35 present in the reaction resin powder. The insoluble reaction resin powder obtained in this manner and free of isocyanate groups can be stored over a relatively long time, depending on requirements, and then converted into

the prepolymeric epoxy resin mixture in a continuous reactor under conditions comparable to those in the second case.

In the process according to the invention, the prepolymeric epoxy resin mixture is cured with a filler-containing pulverulent phenol resin mixture. For the preparation of this phenol resin mixture, for example, the mixing container described above is suitable. A phenol resin or a mixture of phenol resins is melted and is heated to temperatures of up to 160°C while stirring. The filler is then mixed in portions into the phenol resin, and the mixture is devolatilised while stirring. Thereafter, the phenol resin mixture is cooled to room temperature, milled with an impact mill and stored at room temperature in the absence of moisture.

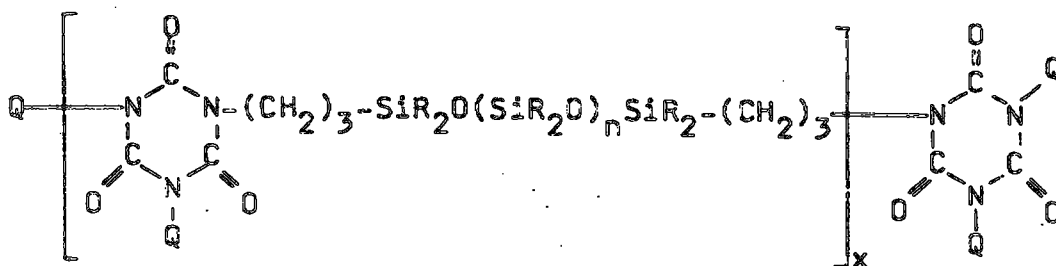
For the preparation of the flame-retardant, free-flowing, phenolically curable epoxy resin moulding material having latent reactivity, the pulverulent prepolymeric epoxy resin mixture and the pulverulent phenol resin mixture are mixed in a molar ratio of phenolic hydroxyl groups to epoxy groups of 0.4 to 1.1; preferably, the molar ratio is 0.6 to 1.0. If necessary, this may be effected with the addition of additives. For example, a frustum mixer having a helical stirrer can be used for mixing of the components, which is carried out at room temperature. The mixing of the components can advantageously also be carried out in a twin-screw extruder which - as described above - has conveying kneading elements in addition to conveying screw elements, for example at temperatures of 90 to 95°C. The extrudate is then cooled and powdered. The free-flowing epoxy resin moulding material obtained in the manner described is stored at room temperature in the absence of moisture.

The coating of electronic components with the epoxy resin moulding material according to the invention is carried out, as a rule, as follows. The free-flowing epoxy resin moulding material is pelletised at room

temperature, and the pellets are heated to temperatures of up to 100°C by a high-frequency heating means. The electronic components are coated with the heated moulding material by the transfer moulding process at mould
5 temperatures of 170 to 190°C and a pressure of 70 to 200 bar, and the moulding material is then cured in the mould for 60 to 120 s. Thereafter, the components are removed from the mould and optionally post-curing of the coating is carried out at temperatures up to 200°C. As an alter-
10 native to pelletising and preheating by a high-frequency heating means, the pulverulent epoxy resin moulding material can be compacted in a plasticator at temperatures of up to 100°C. The production of test specimens, such as sheets and rods, for the determination of mould-
15 ing material properties of the phenolically cured epoxy resin moulding material is also carried out under the same temperature and moulding conditions as for the coating of components.

A reaction resin mixture of polyepoxy resin and
20 polyisocyanate resin is used in the process according to the invention, the polyepoxy resin being a mixture of di- and polyfunctional epoxy resins. The molar ratio of polyfunctional to difunctional epoxy resin is 0.1 to 1.7 and preferably 0.2 to 0.75, based on the epoxy groups. The
25 molar ratio of the epoxy groups to the isocyanate groups (in the reaction resin mixture) is > 1 and preferably 1.5 to 4.0.

In the process according to the invention, suitable epoxy resins, which are part of the polyepoxy
30 resin mixture, are preferably bisphenol A and bisphenol F epoxy resins as well as phenol novolac and cresol novolac epoxy resins or silicone epoxy resins, triglycidyl isocyanurate, tetraglycidyl diamminodiphenylmethane and polyglycidylphosphorus resins. In particular,
35 compounds having the following structure serve as silicone epoxy resins:



where the following is applicable:

n is an integer from 0 to 25,

x is an integer from 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.

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

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

Substituted imidazoles are used as reaction
20 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,
25 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 the di- and polyfunctional epoxy resins.

In particular, phenol and cresol novolac resins,
30 individually or as mixtures, are suitable as a phenol resin. The phenol resin mixtures can also contain

prepolymers of novolac resins and silicone elastomers (silicone-modified phenol resins) or can be mixtures of phenol resins and phosphine oxides.

Suitable fillers are in particular mineral
5 fillers, such as quartz in the form of splinters and/or spherical particles (different particle size distribution), preferably having a particle size of $\leq 100 \mu\text{m}$. Ceramic fillers, such as alumina, and mixtures of ceramic fillers and mineral fillers may also be used. Fibrous
10 fillers, such as short glass fibres, are also suitable.

To reduce tool wear in the preparation and mould wear in the processing and to improve the mould release properties, small amounts of additives may be added to the epoxy resin moulding material. Glyceryl monostearate
15 which can be chemically incorporated and waxes, such as carnauba wax, micronised polyethylene, polyamide and polytetrafluoroethylene are preferably suitable for this purpose. The additives are added to the reaction resin mixture comprising polyepoxy resin and polyisocyanate
20 resin (in the preparation of the prepolymeric epoxy resin mixture) and/or to the phenol resin mixture or - as in the case of micronised thermoplastics - are admixed during mixing of the prepolymeric epoxy resin mixture with the phenol resin mixture. Spherical quartz fillers
25 may also serve for reducing wear.

A process for the preparation of flame-retardant epoxy resin moulding materials according to the invention has not been described to date. However, it is known that moulding materials comprising polyepoxy resins and poly-
30 isocyanate resins can be cured using reaction accelerators. For this purpose, the moulding materials are mixed in a roll mill, for example at temperatures of 80°C , and cured at temperatures up to 180°C directly to give moulding materials (cf.: Japanese Published Application
35 50-059499 and Japanese Published Application 51-128400).

Furthermore, thermally self-curing casting resin mixtures comprising polyepoxy resins and polyisocyanate resins are known (cf.: European Patent specification

0,129,787 and European Patent specification 0,130,454). Here too, the aim is to prepare the cured moulding material directly from the reaction resin mixtures comprising polyepoxy resin and polyisocyanate resin.

5 In the first case (European Patent specification 0,129,787), a process for the preparation of moulding materials for insulated components from rapidly curing reaction resins which can be processed by a method analogous to injection moulding, liquid mixtures (having
10 a viscosity of up to 7,000 mPa.s at 25°C) of essentially oxazolidinone-free polyepoxides and of polyisocyanates (EP-IC resins) - in a batch molar ratio of epoxy groups to isocyanate groups of 1 to 5 - are crosslinked by means of tertiary amines or imidazoles as curing catalysts at
15 gelling temperatures of > 130 to 150°C under a pressure of between 1 and 10 bar and are post-cured at temperatures of 150 to 200°C (with formation of reaction resin moulding materials containing oxazolidinone and isocyanurate rings, so-called OX/ICR moulding materials), the
20 reaction conditions being chosen so that more than 90% of the epoxy and isocyanate groups are converted and that the molar ratio of the oxazolidinone and isocyanurate rings (OX : ICR) in the moulding material is more than 1.

In the second case (European Patent specification
25 0,130,454), a process for the preparation of reaction resin moulding materials (OX/ICR moulding materials) containing oxazolidinone (OX) and isocyanurate rings (ICR), in which mixtures of essentially OX-free polyepoxides and of polyisocyanates (EP/IC resins) are gelled
30 in the presence of a curing catalyst at temperatures of up to 130°C and then post-cured until more than 90% of the epoxy and isocyanate groups are converted, solvent-free, liquid mixtures of polyepoxides and polyisocyanates (having a viscosity of up to 7,000 mPa.s at 25°C) are
35 used in a batch molar ratio of epoxy groups to isocyanate groups of 1 to 5, tertiary amines or imidazoles are used as catalysts and the reaction conditions are chosen so that the molar ratio of oxazolidinone and isocyanurate

rings (OX : ICR) in the moulding material is between 1 and 5.7, i.e. is > 1 .

The process according to the invention differs from the processes described above both in the aim and in the procedure. This is because the intention is to not prepare cured moulding materials but prepolymeric epoxy resin mixtures which can be melted, have latent reactivity, are cured with phenol resin mixtures - with shaping by the transfer moulding process - to give flame-retardant moulding materials and - without the use of halogen-containing flameproofing agents and antimony trioxide - meet the UL 94 V-0 flame resistance rating demanded by the electronics industry at a layer thickness of 1.6 mm.

WO 90/15089 discloses that epoxy-terminated polyoxazolidinones (referred to there simply 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 min 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 then heated to a temperature of 110 to 200°C for the duration of 5 to 180 min. 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.

The polyepoxy compound used in the known process is preferably bisphenol A or tetrabromobisphenol A, and the polyisocyanate compound is 4,4'-methylenabis(phenyl isocyanate) (MDI) or an isomer thereof, polymeric MDI or toluylene diisocyanate. A suitable catalyst (for the reaction of polyepoxy compound and the polyisocyanate compound) is especially an imidazole compound or tetra-

phenylphosphonium bromide; the catalyst 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.

5 For the preparation of the polyoxazolidinones, the catalyst, optionally dissolved in a suitable solvent, is 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
10 temperature and kept there while the polyisocyanate compound is added in a controlled manner, i.e. dropwise.

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

The essential feature of this process is that the
30 oxazolidinone epoxy resins are obtained only when epoxy resins containing OH groups are reacted together with diisocyanates containing NCO groups of different reactivities - under catalysis by phosphonium salts - at about 160°C. For the preparation of the polyepoxides, the
35 bisepoxy resin is heated together with the catalyst under nitrogen to 160°C. The diisocyanate is then added dropwise to the melt at a rate such that a temperature of about 170°C is maintained. After the addition of the

total amount of diisocyanate, stirring is continued at 160°C until the calculated epoxide value has been reached and reactive NCO is no longer detectable.

The preparation described in the two publications mentioned, of epoxy-terminated polyoxazolidinones or of polyepoxides containing oxazolidinone groups, differs fundamentally from the process according to the invention for the preparation of a prepolymeric epoxy resin mixture having latent reactivity, both in the procedure for the preparation of the accelerator-containing reaction resin mixture (comprising polyepoxy resins and polyisocyanate resins) and in the composition of the reaction resin mixture. Thus, in the prior art, as disclosed in particular in the Examples, low catalyst concentrations are used, namely 0.01 to 0.35% (WO 90/15089) or 0.1% (EP 0 296 450 A1), based in each case on polyepoxide. For the preparation of the reactive, curable prepolymeric epoxy resin mixture, however, substantially higher amounts of catalyst are required. 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 the di- and polyfunctional epoxy resins. These high catalyst concentrations are required so that the prepolymeric epoxy resin mixture having latent reactivity can be cured in an industrially relevant time without subsequent acceleration - which is expensive in the case of filler-containing systems.

However, the use of such large amounts of catalysts is possible only if the process according to the invention is used, a complete reaction resin mixture comprising a mixture of di- and polyfunctional epoxy resins, polyisocyanate resin and filler being prepared using imidazoles of the stated art at temperatures of up to 100°C and the prepolymeric epoxy resin mixture having latent reactivity being prepared with this mixture at reaction temperatures up to 200°C. However, it has been found that, at such a high catalyst concentration, it is impossible to heat the epoxy resin mixture according to

the invention to temperatures up to 170°C - corresponding to the prior art - to add the reaction accelerator and to meter in the polyisocyanate resin, since gelled or cured products are formed in this manner, but no soluble, fusible prepolymeric epoxy resin mixtures having latent reactivity are obtained.

The composition of the reaction resin mixture (comprising polyepoxy resin and polyisocyanate resin) in the process according to the invention also differs radically from that of the reaction resin mixtures disclosed in the prior art (WO 90/15089 or EP 0 296 450 A1). This is because, first, the reaction resin mixture according to the invention are mixtures which have a high filler content and, owing to their high viscosity, are as a rule solid at room temperature and for the preparation and handling of which conditions which differ from those for reaction resin mixtures without filler are required. Secondly, mixtures of di- and polyfunctional epoxy resins, for example of bisphenol A epoxy resins with tetrafunctional epoxy resins, such as tetraglycidyl-diaminodiphenylmethane and silicone epoxy resins, are used for the preparation of these reaction resin mixtures having a high filler content. However, such mixtures are not known from the prior art. In addition, neither the particularly suitable reaction accelerator 1-cyanoethyl-2-phenylimidazole nor the silicone epoxy resins - which were important for the processing properties - and tetraglycidyl-diaminodiphenylmethane - which is particularly suitable for increasing the glass transition temperature - are mentioned there.

It was completely surprising and also unforeseeable for a person skilled in the art that, in the process according to the invention for the preparation of the prepolymeric epoxy resin mixture, the use of polyfunctional epoxy resins, such as tetraglycidyl-diaminodiphenylmethane and the stated silicone epoxy resins, and the use of high accelerator concentrations do not lead to curing, i.e. chemical crosslinking, of the reaction resin

mixture comprising polyepoxy resin and polyisocyanate resin - even at reaction temperatures up to 200°C - but instead a prepolymeric epoxy resin mixture which has a long shelf life, is soluble or can be melted, has latent
5 reactivity and can be very readily cured - without subsequent acceleration - is obtained.

It was also found that both the prepolymeric epoxy resin mixture and the phenolically curable epoxy resin moulding material prepared therewith have an
10 outstanding formulation possessing latent reactivity; furthermore, as will be shown subsequently (cf. Table 4), they have a very good shelf life. The fact that the formulation of the phenolically curable epoxy resin moulding material, which formulation possesses latent
15 reactivity, can be adjusted in a controlled manner with regard to the intended use via the concentration - and also via the type - of the reaction accelerator (in the reaction resin mixture comprising polyepoxy and polyisocyanate resin) without the shelf life being limited as
20 a result is also particularly advantageous (cf. in this respect also Table 5). No expensive subsequent acceleration is therefore required for increasing the reactivity of the epoxy resin moulding material. The formulation of the phenolically curable epoxy resin moulding material,
25 which formulation possesses latent reactivity, can additionally be varied via the molar ratio of the phenolic hydroxyl groups to the epoxy groups (cf. Table 6).

A further way of adjusting the reactivity of the
30 phenolically curable epoxy resin moulding material is to use, as a curing component, a phenol resin mixture containing a reaction accelerator. This makes it possible to prepare a very rapidly curing epoxy resin moulding material without the shelf life being adversely affected
35 as a result. A substituted imidazole, such as 1-cyanoethyl-2-phenylimidazole and 2-phenylimidazole or triphenylphosphine preferably serves as such a reaction accelerator. The content of the reaction accelerator in

the phenol resin mixture is 0.5 to 1.5 %, preferably 0.8 to 1.2 %, based on the phenol resin.

The flammability test according to UL 94 shows that the mouldings produced from the epoxy resin moulding material according to the invention achieve the classification V-0 at a layer thickness of ≤ 1.6 mm, said classification being required by the electronics industry. This is surprising because epoxy resin mouldings produced on the basis of cresol novolac epoxy resins and phenol resins (as curing agents) and containing the filler quartz in the same concentration as the epoxy resin moulding material according to the invention do not achieve any classification according to UL 94 V-0 at 1.6 mm layer thickness without the use of brominated flameproofing agents and antimony trioxide, and instead the test specimens undergo complete combustion.

The use of silicone epoxy resins proves to be particularly advantageous in the process according to the invention, both for the preparation and processing of the phenolically curable epoxy resin moulding material and for the properties of the moulding. Thus, in the preparation of the prepolymeric epoxy resin mixture, gentle milling during pulverisation is made possible and, in the processing of the epoxy resin moulding material, the flow behaviour during shaping and the mould release properties of the coated electronic components are improved. For example, the spiral flow length, which is a measure of the flowability of transfer moulding materials under pressure and at high temperature, is substantially improved and increased by up to 20 % by the use of the silicone epoxy resins. Furthermore, the adhesive properties of the phenolically curable epoxy resin moulding material can be adapted to different substrates via the chemical composition and the content of the silicone epoxy resins. This is particularly important for the adhesion to the leadframes of the electronic components, which leadframes are composed of alloys. In the flammability test of the epoxy resin mouldings according

to UL 94, it is found that even small added amounts of silicone epoxy resin improve the flame-retardant behaviour.

Epoxy resin mouldings which are to be suitable
5 for covering and coating electronic components must have excellent mechanical and thermal properties and, even under extreme test conditions, such as thermal cycling with 1000 temperature cycles of -65 to 150°C, must not cause any mechanical/thermal stress which leads to
10 failure of components. The stress behaviour of the epoxy resin mouldings is influenced in particular by the glass transition temperature, the coefficient of linear thermal expansion and the modulus of elasticity. It has been found that the epoxy resin moulding materials according
15 to the invention result in mechanical and thermal properties of the mouldings which meet the requirements for the coating of electronic components (cf. Tables 7 and 8). The fact that mixtures of di- and polyfunctional epoxy resins are used for the preparation of the epoxy
20 resin mixtures proved to be particularly advantageous. This is because these mixtures make it possible substantially to increase the glass transition temperature of the epoxy resin mouldings without the modulus of elasticity and the coefficient of linear expansion being
25 adversely affected. Thus, as will be shown subsequently (c.f. Table 7), glass transition temperatures of > 150°C are achieved in the case of the epoxy resin mouldings according to the invention. If, on the other hand, exclusively difunctional epoxy resins are used, this is
30 not possible. In this case, only glass transition temperatures in the range of 135 to 140°C are in fact obtained.

Even when the processing conditions of the epoxy resin moulding material according to the invention and
35 important properties of the moulding are compared with a moulding material or a moulding according to the prior art, it is found that the demanding requirements of the electronics industry as regard to the processing proper-

ties and the properties of the moulding are met by the epoxy resin moulding material according to the invention (cf. Table 9). The moulding material Nitto HC 10/2 used worldwide served for comparison. This moulding material
5 is a phenolically curable cresol novolac epoxy resin moulding material which contains 70 % of quartz splinters as a filler and is rendered flame-retardant with tetrabromobisphenol A epoxy resin and antimony trioxide as a synergistic agent.

10 Owing to their environment-friendly properties, the epoxy resin mouldings according to the invention also meet further important requirements of the electronics industry for future use. This applies in particular to the suitability of the mouldings for environment-friendly
15 recycling and environmentally compatible disposal by incineration. The environmental compatibility of the epoxy resin mouldings which are flame-retardant without halogen, which compatibility is improved compared with the prior art, is demonstrated by the fact that - in
20 contrast to epoxy resin mouldings containing brominated flameproofing agents and antimony trioxide - no highly corrosive gaseous cleavage products and no decomposition products having a high toxicological and ecological hazard potential are formed during the combustion. In the
25 combustion, for example according to DIN method 53436, the only combustion products found are those which also occur in the case of natural products, such as wool, wood and coal. This ensures that, in the event of a fault, such as a fire or smouldering, there is no environmental
30 pollution over and above the normal case and the procedure for normal domestic waste can be adopted for the disposal by incineration.

 The suitability of the mouldings produced from the epoxy resin moulding material according to the
35 invention for recycling is of particular importance for the electronics industry because considerable amounts of epoxy resin moulding are formed as waste in the coating of components by the transfer moulding process. In

addition, it is intended in the future to recycle the epoxy resin mouldings from the electronics scrap after the metals have been separated off. The epoxy resin mouldings offer good preconditions for recycling because, on the one hand, they can be subjected to high mechanical and thermal stress and have excellent chemical resistance to aggressive chemicals and, on the other hand, in comparison with the prior art, they meet an important requirement, namely environment-friendly material properties.

For the recycling of material wastes in transfer moulding, use as a filler is especially relevant. The technically high-quality fillers can be used in electronics and in electrical engineering generally and for other technologies; for example vehicle technology, and the thermoplastic and thermosetting plastic materials required for this purpose. However, they are also suitable for re-use for the coating of electronic components; for this purpose, the material wastes are milled to the required particle size. The epoxy resin moulding material according to the invention thus provides an environment-friendly covering and coating material which is suitable for the electronics industry, is flame-retardant without halogen and represents substantial progress with regard to the symbiosis of technology and environment in comparison with the prior art.

Embodiments of the invention will now be more particularly described by way of example.

Example 1

30 Preparation of a prepolymeric epoxy resin mixture

255 g of bisphenol A epoxy resin (epoxide value: 5.78 mol/kg), 16.5 g of a silicone epoxide (epoxide value: 1.9 mol/kg), prepared according to Example 9 of European Offenlegungsschrift 0,399,199, 82.5 g of tetra- glycidyldiaminodiphenylmethane (epoxide value: 8.2 mol/kg) and 90 g of an isomer mixture of diisocyanatodiphenylmethane (isocyanate value: 7.9 mol/kg) are introduced into a mixing container, then heated to 80°C

and mixed while stirring and devolatilised. Thereafter, 724.5 g of spherical quartz, 310.5 g of quartz splinters and 15 g of carbon black are added in portions to the mixture while stirring, and devolatilisation is then
5 carried out for 1 h at 80°C while stirring. 5.55 g of 1-cyanoethyl-2-phenylimidazole are metered into the reaction resin mixture, and devolatilisation is then carried out for 15 min while stirring. Thereafter, the temperature of the mixing container is adjusted to 180°C
10 and the reaction resin mixture is reacted while stirring. The course of the reaction is continuously monitored by temperature measurement. The reaction is terminated 4 minutes after reaching the reaction temperature of 130°C in the resin mixture. For this purpose, the mixing
15 container is rapidly cooled by means of a cooling thermostat and the resin mixture is brought to a temperature below 50°C. At this time, no further free isocyanate groups are present, and 40 % of the epoxy groups used have been converted. The melt which solidifies on cooling
20 is coarsely comminuted by the stirrer of the mixing container. This material is then milled at room temperature by means of an impact mill to a particle size of < 200 µm. The resulting free-flowing prepolymeric epoxy resin mixture 1 having latent reactivity (epoxide value:
25 0.86 mol/kg; melting range: 75 to 95°C) is stored at room temperature in the absence of moisture.

Example 2

Preparation of a phenol resin mixture

900 g of cresol novolac resin and 30 g of carbon
30 black are introduced into a mixing container, and the two components are heated to 160°C while stirring. Devolatilisation is then carried out for 1.5 h with further stirring. Thereafter, 1450 g of spherical quartz and 620 g of quartz splinters are mixed in portions into
35 the phenol resin mixture which is at 160°C. Devolatilisation is then carried out again for 1.5 h while stirring. The melt which solidifies on cooling is coarsely comminuted by the stirrer. This material is then

milled at room temperature by means of an impact mill to a particle size of $< 200 \mu\text{m}$. The resulting free-flowing phenol resin mixture 2 (OH value: 2.35 mol/kg) is stored at room temperature in the absence of moisture.

5 Example 3

Preparation of a phenolically curable epoxy resin moulding material

1000 g of the free-flowing prepolymeric epoxy resin mixture according to Example 1 and 282 g of the
10 free-flowing phenol resin mixture according to Example 2 are thoroughly mixed at room temperature in a frustum mixer with a helical stirrer. The resulting free-flowing, phenolically curable epoxy resin moulding material 3 (epoxide value: 0.62 mol/kg; viscosity: 105 Pa.s at
15 162°C; spiral flow length: 67 cm at 175°C) which has latent reactivity and is rendered flame-retardant is stored at room temperature in the absence of moisture.

Examples 4 to 11

Further prepolymeric epoxy resin mixtures are
20 prepared similarly to Example 1. The particular composition of the reaction mixtures which serve for the preparation of the epoxy resin mixtures 4 to 11 are shown in Table 1a (data in parts by weight). Table 1b shows the epoxide value and the melting range in each case, as
25 characteristics of the prepolymeric epoxy resin mixtures (4 to 11).

Examples 12 to 17

Further phenol resin mixtures are prepared similarly to Example 2. The particular composition of the
30 phenol resin mixtures 12 to 17 is shown in Table 2 (data in parts by weight).

Examples 18 to 29

Further phenolically curable epoxy resin moulding materials are prepared similarly to Example 3. The
35 particular composition of the epoxy resin moulding materials 18 to 29 is shown in Table 3.

The epoxide value (EP value) and the viscosity as a function of the storage time are shown in each case in

Table 4 for the prepolymeric epoxy resin mixture 1 and for the phenolically curable epoxy resin moulding materials 3 and 19.

Table 5 shows the effect of type and concentration of reaction accelerator on the viscosity for the phenolically curable epoxy resin moulding material 19. The stated times taken for the initial viscosity (at 175°C) to increase tenfold illustrate the range of variation with regard to imparting latent reactivity to the epoxy resin moulding materials according to the invention.

Table 6 shows the effect of the molar ratio of phenolic hydroxyl groups to epoxy groups (OH:EP) on the viscosity for the phenolically curable epoxy resin moulding materials 3, 19, 20 and 21. As shown by the stated times taken for the initial viscosity (at 175°C) to increase tenfold, the latent reactivity of the epoxy resin moulding materials can be varied via the molar ratio OH:EP.

Table 7 summarises the conditions (temperature, time) in the curing or post-curing of the epoxy resin moulding materials 3, 18, 19, 22, 24, 25, 26, 28 and 29 and the glass transition temperatures of the corresponding mouldings.

In addition to the curing conditions, the coefficient of linear thermal expansion (α) and the modulus of elasticity (E') are shown in Table 8 as further examples of the mechanical/thermal properties for the mouldings produced from the epoxy resin moulding materials 3, 18, 19, 22, 25, 26, 28 and 29.

Table 9 compares flame-retardant EP mouldings which were produced from a commercial moulding material or from an epoxy resin moulding material according to the invention, in each case by transfer moulding. The processing conditions of the moulding materials are shown on the one hand and the properties of the corresponding mouldings on the other hand. The commercial moulding material is moreover rendered flame-retardant by adding

brominated flameproofing agents and antimony trioxide, while the epoxy resin moulding material 27 according to the invention is flame-retardant without halogen.

Example 30

5 Preparation of a prepolymeric epoxy resin mixture

For the preparation of a resin component, 2.55 kg of bisphenol A epoxy resin (epoxide value: 5.78 mol/kg), 0.155 kg of a silicone epoxide (epoxide value: 1.9 mol/kg), prepared according to Example 9 of European
10 Offenlegungsschrift 0,399,199, 0.81 kg of tetraglycidyl-diaminodiphenylmethane (epoxide value: 8.2 mol/kg) and 0.885 kg of an isomer mixture of diisocyanatodiphenylmethane (isocyanate value: 7.9 mol/kg) are introduced into a thermostatable and evacuable mixing container
15 (effective capacity: 20 l); the mixture is then heated to 60°C while stirring. Thereafter, 6.195 kg of spherical quartz, 2.655 kg of quartz splinters, 0.075 kg of polyethylene wax and 0.135 kg of carbon black are added in portions to the mixture while stirring. The mixture is
20 then devolatilised at 60°C for 1 hour while stirring. For the preparation of an accelerator component, 1.05 kg of spherical quartz, 0.45 kg of quartz splinters, 0.015 kg

of carbon black and 55.5 g of 1-cyanoethyl-2-phenylimidazole are homogeneously mixed. The resin component and the
25 accelerator component are simultaneously metered into a twin-screw extruder, the resin component by means of a peristaltic pump at a continuous mass flow rate of 0.042 kg/min and the accelerator component by means of a twin-screw metering apparatus (mass flow rate: 5 g/min).
30 The screws of the extruder are composed of conveying elements, and three conveying kneading blocks, each 28 mm long, are mounted immediately after the feed zone, for homogeneous mixing of the resin component and of the accelerator component. The screw length is 880 mm and the
35 outer screw diameter is 31.8 mm; the five barrel zones of the extruder are adjusted to the following temperature: zone 1 (mixing zone): 81°C, zone 2: 130°C, zone 3: 177°C,

zone 4: 178°C, zone 5: 180°C. The screw speed is 20 min⁻¹, resulting in a melt residence time in the twin-screw extruder of 2.5 min.

The extrudate discharged through a double slot die (cross-section: 2 mm x 20 mm each) is guided along a cooled slide rail, cooled to 43°C and comminuted on a connected elastic take-off belt by 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 30 having latent reactivity (epoxide value: 0.84 mol/kg; melting range: 75 to 95°C) is stored at room temperature in the absence of moisture.

Example 31

15 Preparation of a prepolymeric epoxy resin mixture

A filler-containing reaction resin mixture is prepared similarly to Example 1. 5.55 g of 1-cyanoethyl-2-phenylimidazole are metered into this reaction resin mixture, and devolatilisation is then carried out for 20 10 min while stirring. Thereafter, the reaction resin mixture is reacted by heating the mixing container to 160°C with further stirring; the course of the reaction is continuously monitored by temperature measurement. The reaction is terminated 1 min after solidification of the 25 reaction resin mixture, by cooling the mixing container with a cooling thermostat. The temperature of the reaction resin mixture is brought to below 50°C, with further stirring. As a result of the continuous stirring, the insoluble reaction product which is free of isocyanate groups and has isocyanurate structures is obtained as a 30 free-flowing powder having a long shelf life. This reaction resin powder is fed to a twin-screw extruder via a vibrating trough at a continuous mass flow rate of 30 g/min. The screw length is 880 mm and the outer screw 35 diameter is 31.8 mm; the five barrel zones of the extruder are heated to 160°C. The screw speed is 90 min⁻¹, resulting in a melt residence time in the extruder of 1.5 min.

The extrudate is discharged through a double slot die (cross-section: 2 mm x 20 mm each), cooled to 45°C by direct contact with a cooled slide rail and comminuted on a connected elastic take-off belt by a counter-roller.

5 The material is then milled to a particle size of < 200 µm by means of an impact mill. The resulting free-flowing, curable prepolymeric epoxy resin mixture 31 having latent reactivity (epoxide value: 0.86 mol/kg; melting range: 75 to 95°C) is stored at room temperature

10 in the absence of moisture.

Example 32

Preparation of a phenolically curable epoxy resin moulding material

A phenolically curable epoxy resin moulding

15 material 32 is prepared similarly to Example 3, the composition of said moulding material being shown in Table 3.

The conditions during the curing or post-curing of the epoxy resin moulding material 32 and the glass

20 transition temperature of the corresponding moulding are shown in Table 7, and Table 8 shows the coefficient of linear thermal expansion and the modulus of elasticity, in addition to the curing conditions.

Table 1a

Example	1	4	5	6	7	8	9	10	11
Bisphenol A epoxy resin	17.0	15.1	13.0	15.8	15.3	16.4	15.6	17.5	16.8
Silicone epoxy resin	1.1	0.4	0.8	0.5	0.1	2.1	0.4	-	1.0
Tetraglycidylidiamino- diphenylmethane	5.5	-	4.5	-	5.0	5.3	5.1	5.7	5.4
Cresol novolac epoxy resin	-	8.7	3.7	-	-	-	-	-	-
Triglycidyl isocyanurate	-	-	-	2.5	-	-	-	-	-
Diglycidyl phenyl phosphonate	-	-	-	1.4	-	-	-	-	-
Isomeric mixture of diphenyl- methane diisocyanate	6.0	5.4	4.7	6.5	5.4	5.8	5.5	6.2	5.9
1-Cyanoethyl-2-phenyl- imidazole	0.37	0.36	0.27	-	0.33	0.3	0.36	0.3	0.37
2-Phenylimidazole	-	-	-	0.27	-	-	-	-	-
Spherical quartz	48.3	48.3	49.7	50.4	50.4	69.1	50.4	69.3	-
Quartz splinters	20.7	20.7	22.3	21.6	21.6	-	21.6	-	-
Alumina	-	-	-	-	-	-	-	-	69.0
Carbon black	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Glycerol monostearate	-	-	-	-	0.9	-	-	-	-

Table 1b

Example	Epoxide value mol. kg ⁻¹	Melting range °C
1	0.86	75 to 95
4	0.73	82 to 98
5	0.93	77 to 93
6	0.85	76 to 94
7	0.72	81 to 95
8	0.88	74 to 89
9	0.77	79 to 94
10	0.85	77 to 92
11	0.94	71 to 85

Table 2

Example	2	12	13	14	15	16	17
Phenol novolac resin	-	30.0	7.5	-	-	-	-
Cresol novolac resin	30.0	-	22.5	7.2	27.0	12.5	30.0
sec.-butyl-bis(3-hydroxy-propyl)-phosphine oxide	-	-	-	-	-	17.5	-
silicone-modified phenol resin [*])	-	-	-	22.8	-	-	-
Spherical quartz	48.3	48.3	48.3	48.3	50.4	48.3	-
Quartz splinters	20.7	20.7	20.7	20.7	21.6	20.7	-
Alumina	-	-	-	-	-	-	69.0
Carbon black	1.0	1.0	1.0	1.0	1.0	1.0	1.0

^{*}) prepolymer of alkylphenol novolac resin and silicone elastomer

Table 3

Example	Prepolymeric epoxy resin mixture		Phenol resin mixture		Molar ratio
	No.	parts by weight	No.	Parts by weight	
3	1	78	2	22	1:0.8
18	5	72	15	28	1:1
19	1	74	2	26	1:1
20	1	81	2	19	1:0.6
21	1	86	2	14	1:0.4
22	8	74	2	26	1:1
23	7	75	15	25	1:1
24	9	75	15	25	1:1
25	10	74	2	26	1:1
26	4	78	2	22	1:0.8
27	1	73	2	27	1:1
28	1	73	14	27	1:1
29	11	78	17	22	1:0.8
32	30	78	2	22	1:0.0

Table 4

Storage time in months*)	Epoxy resin mixture 1		Epoxy resin moulding material 3		Epoxy resin moulding material 19	
	EP value mol. kg ⁻¹	viscosity Pa.s / °C	EP value mol. kg ⁻¹	viscosity Pa.s / °C	EP value mol. kg ⁻¹	viscosity Pa.s / °C
0	0.86	95 / 168	0.62	105 / 164	0.61	125 / 161
0.5	0.83	95 / 168	0.65	110 / 168	0.62	140 / 160
1	0.82	95 / 168	0.64	90 / 169	0.61	110 / 164
2	0.85	100 / 165	0.63	110 / 168	0.62	100 / 166
3	0.83	95 / 167	0.63	105 / 168	0.61	105 / 165
4	0.84	100 / 165	0.64	100 / 169	0.60	120 / 167
5	0.85	95 / 168	0.62	115 / 168	0.61	120 / 168
6	0.85	95 / 168	0.62	110 / 169	0.62	120 / 168

*) At room temperature and in the absence of moisture

Table 5

Reaction accelerator	Contents*) %	Time taken to increase to 10 times initial viscosity at 175°C in s
2-Phenylimidazole	0.7	109
2-Phenylimidazole	0.9	85
2-Ethyl-4-methylimidazole	0.7	103
1-Cyanoethyl-2-phenylimidazole	0.8	89
1-Cyanoethyl-2-phenylimidazole	1.0	69
1-Cyanoethyl-2-phenylimidazole	1.25	54
1-Cyanoethyl-2-phenylimidazole	1.5	48

*) Based on the filler-free reaction resin mixture
comprising polyepoxy resin and polyisocyanate resin

Table 6

Epoxy resin moulding material No.	Molar ratio OH : EP	Time taken to increase to 10 times initial viscosity at 175°C in s
3	0.8 : 1	59
19	1.0 : 1	68
20	0.6 : 1	47
21	0.4 : 1	40

Table 7

Epoxy resin moulding material No.	Curing °C / min	Post-curing °C / min	Glass transition temperature*) °C
3	190 / 1	190 / 240	161
3	180 / 2	190 / 240	157
3	170 / 3	175 / 480	158
18	175 / 1.5	190 / 240	160
19	190 / 1	190 / 240	156
22	180 / 2	190 / 240	161
22	170 / 3	180 / 240	155
24	175 / 1	220 / 240	164
25	180 / 2	200 / 240	154
26	175 / 1	190 / 240	156
28	190 / 3	190 / 240	153
29	175 / 1.5	190 / 240	158
32	185 / 1.5	190 / 240	154

*) TMA (thermomechanical analysis)

Table 8

No.	Epoxy resin moulding material	Curing °C / min	Post-curing °C / min	$\alpha_1^1)$ $10^{-6}.K^{-1}$	$\alpha_2^2)$ $10^{-6}.K^{-1}$	Modulus of Elasticity ³⁾ in $N.mm^{-2}$	
						50°C	100°C
3	190 / 1	190 / 240	74	20	10840	10360	
3	170 / 3	175 / 480	71	18	11100	10570	
18	175 / 1.5	190 / 240	68	18	10500	9700	
19	190 / 1	190 / 240	75	19	11230	10640	
22	180 / 2	190 / 240	68	19	10300	9800	36
22	170 / 3	180 / 240	71	20	10100	9300	
25	180 / 2	200 / 240	71	18	11360	10810	
26	175 / 1	190 / 240	72	19	10340	9840	
28	190 / 3	190 / 240	79	19	8200	6600	
29	175 / 1.5	190 / 240	100	27	9800	8980	
32	185 / 1.5	190 / 240	75	19	10950	10420	

1) mean value in the temperature range 50 to 100°C

2) mean value in the temperature range 200 to 250°C

3) DMA (dynamic mechanical analysis), 1 Hz

Table 9

Moulding material Epoxy resin
(commercial) moulding material 27

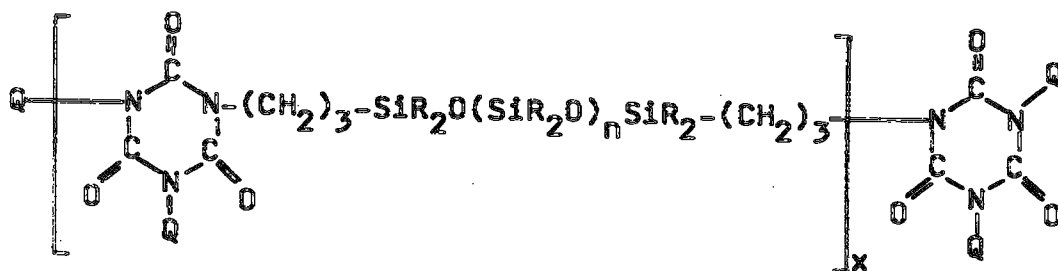
Curing (in the mould)	°C / min	170-190 / 1-3	170-190 / 1-3
Post-curing (in the oven)	°C / min	175-190 / 240-360	175-225 / 120-480
Combustion behaviour	UL 94 / mm	V-O / 1.6	V-O / 1.6
Glass transition temperature ¹⁾	°C	165-166	156-161
Coefficient of expansion			
α ₁ : 50 to 100°C	10 ⁻⁶ .K ⁻¹	18-20	18-20
α ₂ : 200 to 250°C	10 ⁻⁶ .K ⁻¹	63-66	69-73
Modulus of elasticity ²⁾			
at 50°C	N.mm ⁻²	11500-11600	10800-11700
100°C	N.mm ⁻²	10400-10500	10100-11100
200°C	N.mm ⁻²	2400-2700	660-860
Glass transition temperature	N.mm ⁻²	8500-8800	8600-9400
Decomposition temperature ³⁾	°C		355-357368-374

1) TMA, 5 K/min
 2) DMA, tensile stress, 5K/min, 1 Hz
 3) TGA, 2 K/min, 5 % mass loss (N₂) (TGA = thermogravimetric analysis)



Patent Claims

1. Process for the preparation of a flame-retardant, free-flowing phenolically curable epoxy resin moulding material having latent reactivity for coating electronic components, characterised in that a prepolymeric epoxy resin mixture free of isocyanate groups and having latent reactivity is prepared in powder form from a filler-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 epoxide groups to isocyanate groups of > 1 - using substituted imidazole as a reaction accelerator in a concentration of 0.5 to 2.5 % based on the polyepoxy resin - at reaction temperatures up to 200°C, and that the epoxy resin mixture is mixed with a pulverulent, filler-containing phenol resin mixture in a molar ratio of epoxy groups to phenolic hydroxyl groups of 1:0.4 to 1:1.1, optionally with the addition of additives.
2. Process according to Claim 1, characterised in that the epoxy resin used is a bisphenol A or bisphenol F epoxy resin, a phenol novolac or cresol novolac epoxy resin, triglycidyl isocyanurate, tetraglycidyl diamino-diphenylmethane, a polyglycidylphosphorus resin or a silicone epoxy resin of the general formula



where the following is applicable:

n is an integer from 0 to 25,

x is an integer from 0 to 3,

R = alkyl or aryl and

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

in which n and R have the above-mentioned meaning



and R' is an epoxy functional radical having 6 carbon atoms.

3. Process according to Claim 2, characterised in that the content of silicone epoxy resin is up to 20 %, preferably 1 to 7 %, based on the filler-free reaction resin mixture comprising polyepoxy resin and polyisocyanate resin.
4. Process according to any of Claims 1 to 3, 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.
5. Process according to one or more of Claims 1 to 4, 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.
6. Process according to one or more of Claims 1 to 5, characterised in that, in the reaction resin mixture, the molar ratio of epoxy groups to isocyanate groups is 1.5:1 to 4:1.
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.
8. Process according to one or more of Claims 1 to 7, characterised in that the content of reaction accelerator is 1.0 to 1.8 %, based on polyepoxy resin.
9. Process according to one or more of Claims 1 to 8, characterised in that phenol or cresol novolacs or mixtures thereof are used as the phenol resin.
10. Process according to one or more of Claims 1 to 9, characterised in that the phenol resin mixture contains a reaction accelerator, the content of the reaction accelerator being 0.5 to 1.5 %, preferably 0.8 to 1.2 %, based on the filler-free phenol resin mixture.
11. Process according to one or more of Claims 1 to 10, characterised in that mineral fillers, such as quartz, and/or ceramic fillers, such as alumina, are



used.

12. Process according to one or more of Claims 1 to 11, characterised in that the molar ratio of epoxy groups to phenolic hydroxyl groups in the curable epoxy resin
- 5 moulding material is 1:0.6 to 1:1.

THIS SHEET HAS BEEN
REPLACED

Abstract

In a process for the preparation of a flame-retardant, free-flowing, phenolically curable epoxy resin moulding material having latent reactivity for coating electronic components, a prepolymeric epoxy resin mixture free of isocyanate groups and having latent reactivity is prepared in powder form from a filler-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 - using substituted imidazole as a reaction accelerator in a concentration of 0.5 to 2.5 %, based on polyepoxy resin - at reaction temperatures up to 200°C, and the prepolymeric epoxy resin mixture is mixed with a pulverulent, filler-containing phenol resin mixture in a molar ratio of epoxy groups to phenolic hydroxyl groups of 1:0.4 to 1:1.1, optionally with the addition of additives.

This Sheet Has Been Replaced



P-001-0.0

Substitute sheet - 21 June 1996

Abstract

Process for the preparation of a flame-retardant epoxy resin moulding material

In a process for the preparation of a flame-retardant, free-flowing, phenolically curable epoxy resin moulding material having latent reactivity for coating electronic components, a prepolymeric epoxy resin mixture free of isocyanate groups and having latent reactivity is prepared in powder form from a filler-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 - using substituted imidazole as a reaction accelerator in a concentration of 0.5 to 2.5 %, based on polyepoxy resin - at reaction temperatures up to 200°C, and the prepolymeric epoxy resin mixture is mixed with a pulverulent, filler-containing phenol resin mixture in a molar ratio of epoxy groups to phenolic hydroxyl groups of 1:0.4 to 1:1.1, optionally with the addition of additives.

