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- (71) **Applicant (for all designated States except US):** **EVONIK DEGUSSA GMBH** [DE/DE]; Rellinghauser Straße 1-11, 45128 Essen (DE).
- (72) **Inventors; and**
- (71) **Applicants (for US only):** **NOWAK, Rüdiger** [DE/DE]; Wollbacherstraße 10, 79400 Kandern-Egerten (DE). **SCHLOSSER, Thomas** [DE/DE]; Blumenacker 18, 79594 Inzlingen (DE). **CONN, Rodney, C** [US/US]; 39 Cherokee Street, Emmaus, Pennsylvania 18049 (US).

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(54) **Title:** REINFORCED EPOXY RESIN ADHESIVE

(57) **Abstract:** The present invention relates to an improved epoxy resin adhesive, in particular to a method for preparing such improved epoxy resin adhesive and an improved method for reinforcing, thickening and rendering thixotropic an epoxy resin adhesive.



Reinforced Epoxy Resin Adhesive

The present invention relates to an improved epoxy resin adhesive, in particular to a method for preparing such improved epoxy resin adhesive and an improved method for reinforcing, thickening and rendering thixotropic an epoxy resin adhesive.

- 5 Adhesives consist of high-polymeric substances having as good strength as possible. Most adhesives contain high-molecular-weight organic substances as the basic raw materials or reactive organic compounds which are precursors of polymeric substances and which react during the adhesive and sealing process to form polymers. Adhesives are based e.g. on epoxy resins, polyurethane resins or vinyl ester resins (Ullmanns Enzyklopädie der technischen Chemie, 4th Edition, Volume 10 14, page 227, 1997).

- Epoxy resin adhesives (see e.g. Ullmann's Encyclopedia of Industrial Chemistry, Volume A1, page 241, 5th ed., 1985) are based on epoxy resins (see e.g. Ullmann's Encyclopedia of Industrial Chemistry, Volume A9, page 547-563, 5th ed., 1987) which 15 are produced for example by condensation of 2,2-bis-(4-hydroxyphenyl)propane, also known as bisphenol A, and epichlorohydrin (1-chloro-2,3-epoxy-propane) in a basic environment. Depending on the equivalents of both educts that are used, glycidyl ethers of varying molar mass are produced. In recent years epoxy resins based on bisphenol F (bis(4-hydroxyphenyl)methane), novolak epoxy resins and cycloaliphatic 20 and heterocyclic epoxy resins have also gained importance. Since epoxy resins alone are poor film formers, molecule enlargement by means of suitable crosslinking agents is required. Polyamines, polyaminoamides, carboxylic anhydrides and dicyandiamides, for example are used as crosslinking agents for epoxy resins. Among amine hardeners a distinction is made between aliphatic, cycloaliphatic, 25 aromatic and araliphatic polyamines. Curing takes place without elimination of reaction products. In this process a reactive hydrogen atom is generally added to the epoxy group to form a hydroxyl group.

- In order to improve a number of commercially valuable mechanical properties, such as hardness, tensile strength, stress values and other measurable properties, finely 30 distributed fillers in the form of a hard phase surrounded by the softer epoxy adhesive polymer are added to the adhesives. One of the most commonly used fillers

in epoxy adhesive is amorphous silicon dioxide e.g. in form of evaporated silicon dioxide sols (DE 10 2005 018 671 A1, WO 02/083776 A1) or fumed (pyrogenic) silica (Evonik Industries, Technical Bulletin Fine Particles No. 27-1-October-2009). By modification of the surface of the silicon dioxide particles both silicon dioxide forms
5 can be rendered hydrophobic. This is achieved by reaction of the silanol groups on the silicon dioxide particle surface with suitable compounds, such as alkylchlorosilanes (e.g. dimethyldichlorosilane) or polydimethylsiloxanes (Evonik Industries, Technical Bulletin Fine Particles No. 27-1-October-2009). Whereas the silicon dioxide produced by sol evaporation consists of discrete non-aggregated
10 particles and provides epoxy resins with a relatively low viscosity (DE 10 2005 018 671 A1, WO 02/083776 A1), the silicon dioxide particles of fumed silica develop aggregates which reversibly join together to form agglomerates (Evonik Industries, Technical Bulletin Fine Particles No. 27-1-October-2009).

Fumed silica, also known as pyrogenic silica, usually is used as thickener and
15 thixotrope in epoxy adhesives. Hydrophobic pyrogenic silicas are very effective thixotropic agents in comparison to hydrophilic pyrogenic silicas. Adhesive systems can be made more stable in storage with hydrophobic fumed silicas than with hydrophilic, fumed silicas (Evonik Industries Schriftenreihe Pigmente (2009) No. 27 and No. 54).

20 According to the current state of technology, especially fumed silicas treated with polydimethylsiloxane fluid (PDMS) are very efficient thickeners and thixotropes for epoxy resins and epoxy adhesives. Furthermore, these PDMS treated fumed silicas are very hydrophobic and therefore give additional advantages in the polar epoxy adhesives like improved storage stability and water resistance. However, sometimes
25 adhesive formulators want to avoid silicone oil in their formulation caused by the PDMS treated silicas, which can adversely influence adhesion and levelling of the epoxy adhesive. Also, sometimes adhesive formulators want to reduce the long incorporation time of the PDMS treated fumed silicas in epoxy adhesives.

WO 2004/005393 A1 provides a method of reinforcing unsaturated polyester resins,
30 vinyl ester resins, and acrylic resins wherein pyrogenically prepared silica which has been surface-modified with a silane containing methacrylic groups is mixed with the uncrosslinked resin. Such kind of silica can e.g. be obtained by treatment of

pyrogenically prepared silicas (e.g. with BET specific surface areas from 20 to 380 m²/g, e.g. 200±25 m²/g) with a methacryloxytrialkoxysilane, e.g. methacryloxypropyltrimethoxysilane (3-trimethoxysilylpropyl 2-methylprop-2-enoate) as disclosed in US 2002/0077407 A1, US 2002/0077388 A1, and US 2002/0077381 A1. Since the silicas are surface-modified with a silane bearing already the desired reactive cross-linking groups prior to mixing with the uncrosslinked resin this method of reinforcing liquid thermosets avoids the treatment with silanes bearing the reactive groups during mixing of the filler into the polymer and, hence, the production of unwanted cleavage products such as e.g. alcohols in the resin mixture. In this case the crosslinking of the silica filler particles with the resin is achieved by a radical polymerisation. Therefore, such surface-modified silica is not suitable for improving reinforcement of epoxy resin systems.

JP 01011122 A (English abstract) discloses the preparation of a reinforced epoxy resin composition suitable for sealing electronic parts which is obtained by blending an epoxy resin, a curing agent and natural quartz previously treated with an orthosilicate (e.g. tetramethoxysilane) and a specific silane coupling agent (e.g. 3-glycidyloxypropyltrimethoxysilane/3-(2,3-epoxypropyloxy)propyl-trimethoxysilane). However, natural quartz powder is a crystalline product with particle sizes in the micrometer range allowing high filling grades (up to 70 % by weight) in epoxy resin compositions. Therefore, natural quartz powder, even silanised, has a low thickening effect in epoxy resin systems. Such epoxy resin systems are particularly suitable for sealing electronic parts or for use in road markings. However, due to its low thickening effect natural quartz is not suitable for use in particular adhesives.

JP 2006328349 A discloses particulate fillers for epoxy resin compositions providing among other a low viscosity even if the average particle diameter is made small. Therefore, such fillers are particularly useful as a sealing material for protecting small electronic parts, e.g. as a semiconductor sealing material or a sealing agent for a flat panel display. The filler comprises a powder constituted of composite particles with an average particle diameter of 0.01 to 10 µm the surfaces of which are covered with a crosslinkable polymer having an epoxy group. The particles are obtained by allowing an inorganic powder such as crystalline, fused or precipitated silica or silica obtained by a sol gel method to absorb a crosslinkable and polymerizable

composition containing an epoxy group-containing monomer, e.g. glycidyl-methacrylate (2,3-epoxypropyl 2-methylprop-2-enoate). In the case of an epoxy resin composition it is proposed to use this filler in a quantity of 10 to 2000 parts by mass relative to 100 parts by mass of an epoxy resin. The lowest proposed filler concentration corresponds to 9.1 % by weight. However, due to its low viscosity such highly filled epoxy resins are not suitable for use as adhesives e.g. in the area of seals in glass facades, joints in shipbuildings and wind energy stations.

The JP 2006328349 A document further discloses a spherical silica treated with 3-glycidylxypropyltrimethoxysilane having a carbon content of 2.1 % by weight, a specific BET surface of $19 \text{ m}^2/\text{g}$ and an average particle diameter of $0.16 \text{ }\mu\text{m}$ (Comparative Example 1) which shows in an epoxy resin at a high filling grade (mass ratio of epoxy resin to treated spherical silica of 1:1) at 30° C a viscosity of 9.3 Pa s at a shear rate of 6 s^{-1} and a thixotropic index (i.e. the quotient of the viscosity at a shear rate of 6 s^{-1} and the viscosity at a shear rate at 60 s^{-1}) of 1.2 after preparation and a viscosity of 25.0 Pa s at a shear rate of 6 s^{-1} and a thixotropic index of 0.74 after standing for 30 days. However, such low viscosities at very high filling grades are only useful for application of such epoxy resin compositions as sealing materials for protecting small electronic parts, e.g. as a semiconductor sealing material or a sealing agent for a flat panel display. For such applications it is of essential importance for the sealing material to have a low viscosity in order to easily fill ultrafine voids and to ensure good moulding properties. Therefore, such kind of fillers are not suitable for use in adhesives in the area of glass facades, joints in shipbuildings and wind energy stations where adhesives have to be thickened and thixotropic and must have thixotropic-indices of higher than 2 in order to achieve both good non-sagging properties, especially at declined surfaces, and good processabilities. A further disadvantage of such an epoxy resin composition is its increase in viscosity after storage. An important property of adhesives is a constant viscosity even after long term storage (e.g. 30 days).

US 2002/0077407 A1 (EP 1 199 335 A1) and US 6,197,863 B1 disclose the surface modification of pyrogenically produced silicas with a BET specific surface area from 25 to $380 \text{ m}^2/\text{g}$, particularly of a pyrogenically produced silica with a BET specific surface area of $200 \pm 25 \text{ m}^2/\text{g}$ by treatment with 3-glycidylxypropyl-trimethoxysilane

(3-(2,3-epoxypropyloxy)propyl-trimethoxysilane). According to US 2002/0077407 A1, US 2002/0077388 A1, and US 2002/0077381 A1 such pyrogenically produced and surface-modified silicas, optionally structurally modified by milling, can be used as reinforcing fillers in light-curing lacquers in order to improve scratch resistance.

- 5 US 3,702,783 proposes coating siliceous materials, such as glass fibers, with a mixture of a 3-glycidoxypropyltrialkoxysilane and a methyltrialkoxysilane for improving the bonding of epoxy resins to the siliceous material.

US 3,328,339 proposes as reinforcing fillers for linear or crosslinking polymers siliceous materials, e.g. fumed silicas or silicas obtained by evaporation of a silica
10 sol, which have been surface-modified by epoxy containing coupling reagents, such as 3,4-epoxybutyl-tricyclohexyloxysilane. Such surface-modified silicas may be suitable for reinforcing epoxy resins.

With the object of providing particulate metal oxides that have only a minor influence on the viscosity and other rheological properties of liquid media, WO 2008/077814
15 A2 (US 2010/0021725 A1 = DE 10 2006 061057 A1) discloses pyrogenically prepared silicas (e.g. having a BET specific surface of 300 m²/g) which have been surface modified with a silicone resin coating, obtained essentially by reacting fumed silica with two surface-modifying agents, namely hexamethyldisiloxane and 3-glycidyloxypropyl-trimethoxysilane (3-(2,3-epoxypropyloxy)propyl-trimethoxysilane).
20 However, these silicas are characterized by a low thickening effect in liquid systems (e.g. according to Example 5/Table 1 of the document a relative viscosity of 2 at 25°C and at a sheer rate of 10 s⁻¹ when dispersed at a filling grade of 15 % by weight until a constant grindometer value in a bisphenol A epoxy resin having a viscosity of 8 Pas). Such silicas can e.g. be used at high filling grades for the preparation of
25 adhesives and sealing material on epoxy basis of low viscosities and thus excellent processability for particular purposes.

Reinforcing, but also only poorly thickening and poorly thixotropic effects in epoxy resins are achieved by non-aggregated surface-modified silicon dioxide nanoparticles as disclosed in US 2004/0147029 A1 and DE 10 2005 018 671 A1. Such non-
30 aggregated silicon dioxide nanoparticles are obtained essentially by evaporation of a silicon dioxide sol and subsequent surface modification with e.g. 3-

glycidoxypropyltrimethoxysilane. In order to improve the thixotropy of the epoxy resin, the resin system has to be complemented by pyrogenic silicon dioxide (fumed silica) in addition to the non-aggregated nanoparticles, as disclosed e.g. in US 2007/0191556 A1.

- 5 The present invention provides an improved epoxy resin adhesive, in particular a method for preparing such improved epoxy resin adhesive and a method for reinforcing, thickening and rendering thixotropic an epoxy resin adhesive.

It is further object of the present invention to avoid the adverse influence on adhesion and levelling of epoxy adhesives due to the silicone oil content if PDMS treated
10 fumed silica grades are used as fillers.

Furthermore, it is object of the present invention to provide a method to formulate fumed silica thickened and thixotropic epoxy structural adhesives with shortened manufacturing time, especially with improved wet-in behaviour and thus reduced incorporation time of the fumed silicas in the epoxy adhesives, as well as to improve
15 storage stability of epoxy resin adhesives in a humid or even wet environment and to reduce the incorporation time in liquid epoxy adhesives at low silica filling grades.

More particularly, the object of the present invention is an epoxy resin adhesive obtainable by combining an epoxy resin, 1 to 15 % by weight, preferably 1 to 9 % by weight or 3 to 6 % by weight of surface-modified fumed silica and a curing agent, the
20 surface-modified fumed silica bearing 3-glycidyloxypropylsilyl groups fixed on the surface and having a specific surface area (BET) of $145 \pm 20 \text{ m}^2/\text{g}$, a carbon content from about 3.5 to about 6.5 % by weight, a tapped density (measured according to DIN EN ISO 787/11) of 30 to 100 g/l, preferably 40 to 70 g/l, particularly preferably of 60 g/l, a moisture content (2 hours at 105°C) of smaller or equal to 1.0 % by weight
25 (measured in accordance to DIN EN ISO 787/2, ASTM D 280), and a pH (in 4 % aqueous dispersion, in accordance to DIN EN ISO 787/9, ASTM D 1208) from about 4.0 to about 6.0.

The present invention also concerns a kit of parts comprising an epoxy resin, a curing agent and fumed silica bearing 3-glycidyloxypropylsilyl groups fixed on the
30 surface and having a specific surface area (BET) of $145 \pm 20 \text{ m}^2/\text{g}$, a carbon content

from about 3.5 to about 6.5 % by weight, a tapped density (measured according to DIN EN ISO 787/11) of 30 to 100 g/l, preferably 40 to 70 g/l, particularly preferably of 60 g/l, a moisture content (2 hours at 105° C) of smaller or equal to 1.0 % by weight (measured in accordance to DIN EN ISO 787/2, ASTM D 280), and a pH (in 4 % aqueous dispersion, in accordance to DIN EN ISO 787/9, ASTM D 1208) from about 4.0 to about 6.0. The silica is preferably already dispersed in the epoxy resin.

Furthermore, the present invention provides a method for preparing the epoxy resin adhesive comprising the following steps:

(a) mixing a hydrophilic fumed silica having a specific surface area (BET) of 200 ± 25

m²/g, a tapped density (measured according to DIN EN ISO 787/11) of 30 to 100 g/l, preferably of 40 to 70 g/l, more preferably of 50 g/l, an average primary particle size of about 12 nm, a moisture content (2 hours at 105° C) of smaller or equal to 1.5 % by weight (measured in accordance to DIN EN ISO 787/2, ASTM D 280), and a pH (in accordance to DIN EN ISO 787/9, ASTM D 1208) from about 3.7 to about 4.7 first with water or dilute acid and then with 3-glycidyloxypropyltrimethoxysilane or 3-glycidyloxypropyltriethoxysilane or 3-glycidyloxypropyltripropoxysilane as the surface-modifying agent, subjecting the mixture to heat treatment at a temperature of from 100 to 400 °C over a period from 1 to 6 hours,

(b) dispersing 1 to 15 % by weight, preferably 1 to 9 % by weight or 3 to 6 % by weight of the fumed silica bearing 3-glycidyloxypropylsilyl groups fixed on the surface obtained in step (a) to an epoxy resin and

(c) mixing the dispersion of step (b) with a curing agent.

The starting material, the fumed hydrophilic silica, also known as pyrogenic silica, is prepared by flame hydrolysis of volatile silicon compounds, such as, for example tetrachlorosilane, methyltrichlorosilane or the like. They are known e.g. from Ullmann's Enzyklopädie der technischen Chemie 4th edition, Volume 21, page 464 (1982). Nowadays, several fumed hydrophilic silicas with various different physical and chemical properties, e.g. different BET surfaces or average primary particle sizes, are commercially available.

The epoxy resin adhesive can either be a 1-component (1K) or a 2-component (2K) epoxy resin adhesive. The epoxy resin may comprise further substances such as

fillers, flexibilisators, thixotropic agents, air releasing agents. 1-component epoxy resin adhesives already contain epoxy resin, the curing agent in the desired ratio and the fumed silica according to the present invention. Curing usually occurs at elevated temperatures. A typical curing agent for 1-component epoxy resin adhesives is e.g.

5 dicyanamide. In case of 2-component epoxy resin adhesives curing occurs by mixing the epoxy resin comprising the fumed silica according to the present invention and the curing agent at room temperature. In this case also the curing agent component may comprise additives such as fillers or thixotropic agents. Typical curing agents for 2-component epoxy resin adhesives are e.g. polyamines, such as diethylenetriamine.

10 The present invention also concerns the use of fumed silica bearing 3-glycidyloxy-propylsilyl groups fixed on the surface and having a specific surface area (BET) of $145 \pm 20 \text{ m}^2/\text{g}$, a carbon content from about 3.5 to about 6.5 % by weight, an approximate tapped density (measured according to DIN EN ISO 787/11) of 30 to 100 g/l, preferably 40 to 70 g/l, particularly preferably of 60 g/l, a moisture content (2
15 hours at 105°C) of smaller or equal to 1.0 % by weight (measured in accordance to DIN EN ISO 787/2, ASTM D 280), and a pH (in 4 % aqueous dispersion, in accordance to DIN EN ISO 787/9, ASTM D 1208) from about 4.0 to about 6.0 for reinforcing, thickening and rendering thixotropic an epoxy resin adhesive. The fumed silica containing epoxy functional groups shows an improved incorporation and wet-in
20 behaviour in epoxy resins compared to standard fumed silicas used in epoxy resins.

The present invention also concerns a method for improving the storage stability and bond strength of an epoxy resin adhesive under wet environmental conditions and/or after water immersion.

Applications for these described fumed silica thickened and thixotropic epoxy based
25 structural adhesives are bonded joints in metals and plastics, usually with a silica concentration of 1 to 6 % by weight, bonded joints and seals in glass facades for hotels, bonded joints in shipbuildings, plant construction, wind energy station, especially bonded rotor blades, and automotive constructions, in particular in the formulation as epoxy bonding pastes with a silica concentration of 5 to 9 % by
30 weight, preferably 5 to 8 % by weight.

It has been found, that the epoxy resin adhesive filled with the fumed silica and

treated with the 3-glycidyloxypropyltrialkoxysilane performed significantly better regarding adhesive strength after water immersion than fumed silicas treated with polydimethylsiloxanes. The current technology is that the use of highly hydrophobic fumed silicas in epoxy resins result in further performance enhancements, especially water resistance of the adhesives. Especially, a high degree of hydrophobicity is required to reduce the moisture intrusion into the bond line of the adhesives.

Traditionally, this has been accomplished by using fumed silica treated with polydimethylsiloxane (PDMS). The test results presented in example 1 show that the fumed silica, treated with a 3-glycidyloxypropyltrialkoxysilane is a better choice than PDMS treated fumed silica. Due to the nature of the silane and the residual silanol content, the fumed silica with the epoxy silane is more hydrophilic than hydrophobic.

An increase in strength in a reactive resin may be explained by a continuation in the cure mechanism, often called post-cure. This may be a result of continued reaction of residual epoxy groups of the epoxy silane treated fumed silica both with the epoxy resin adhesive and the substrate. It may also be due to changes in the lattice network of the epoxy resin.

Furthermore, this 3-glycidyloxypropyltriethoxysilane treated fumed silica is also a better option for formulators who wish to avoid silicone oil caused by the PDMS treated fumed silica in their formulation, which can adversely influence adhesion and levelling of the adhesive.

Also the incorporation time of the epoxy silane treated fumed silica was significantly shorter compared to PDMS treated fumed silica shown in example 2.

The incorporation time is understood to be the time during incorporation using a mixer in which the fine-particle fumed silica has completely disappeared from the surface of the binder and is wetted with the binder.

Using that 3-glycidyloxypropyltriethoxysilane treated fumed silica it is possible to reduce the time needed to produce thickened and thixotropic epoxy resins as compared to standard used polydimethylsiloxane (PDMS) or octylsilane treated silicas. This time saving in the production of thickened and thixotropic epoxy resins can reduce costs.

Through the reduction that is achieved in the incorporation time for the 3-glycidyloxypropyltriethoxysilane treated fumed silica the temperature increase during the incorporation process is also reduced. This reduction in the temperature increase is especially advantageous for highly viscous, heat-sensitive structural adhesives based on epoxy resins, which are produced in large batches with high-speed production mixers or similar dispersing units, since overlong incorporation of the silica into the highly viscous polymer systems can lead to localised overheating, which can damage the polymer system. This risk is reduced by the shorter incorporation time for these 3-glycidyloxypropyltriethoxysilane treated fumed silicas compared to PDMS or octylsilane treated fumed silicas. The reduction in the temperature increase during the incorporation brings also a reduction in the emission of toxic, highly volatile substances, such as styrene, epichlorohydrin or polyamines, allowing the costs for large-scale extraction plants to be reduced.

Examples

The specific surface area (BET, see S. BRUNAUER, P. H. EMMETT, E. TELLER, J. Am. Chem. Soc. 60, 309 (1938)) of the pyrogenic silicas has been determined according to DIN 66131.

The carbon content of the silicas has been determined by a method which is suitable for the determination of the carbon content in metals, metal oxides and inorganic matrices in a range of 0.001-90% (w/w). The sample should be in form of small pieces, ideally in the form of a powder. After weighing the sample in a ceramic crucible combustible material is added and the sample is heated in a HF induction furnace. Carbon present in the sample is oxidized to CO₂ and is quantified by infrared detectors. The elemental analyzers used were a LECO CS 244 or a LECO CS 600 C. The correctness of the determination is ensured by calibration with certified reference samples. The detection limit for carbon is 10 µg/g.

The tapped density of the pyrogenic silicas has been measured according to DIN EN ISO 787/11.

The moisture content of the pyrogenic silicas (2 hours at 105° C) has been measured in accordance to DIN EN ISO 787/2, ASTM D 280.

The pH value of the pyrogenic silicas has been measured in 4 % aqueous dispersion in accordance to DIN EN ISO 787/9, ASTM D 1208.

Table 1: Physical and chemical properties of the fumed silicas

	Silica 1 (comparative)	Silica 2 (comparative)	Silica 3 (used according to the invention)	Silica 4 (comparative)
Commercially available under the brand name	AEROSIL® 200 Evonik Industries AG	AEROSIL® R 202 Evonik Industries AG	n. a.	AEROSIL® R 805 Evonik Industries AG
Surface properties	hydrophilic fumed silica	hydrophobic fumed silica, treated with polydimethylsilo- xane fluid (PDMS)	fumed silica, treated with 3- glycidylloxypro- pyltrimethoxy- silane	hydrophobic fumed silica, treated with octyltrimethoxy- silane
Specific surface area (BET) [m ² /g]	200 ± 25	100 ± 20	145 ± 20	150 ± 25
Carbon content [% by weight]	n. a.	3.5 - 5.0	3.5 - 6.5	4.5 - 6.5
Tapped density [g/l]	50±10	50±10	60±10	50±10
average primary particle size [nm]	12	14	12	12
Moisture content [% by weight]	≤ 1.5	≤ 0.5	≤ 1.0	≤ 0.5
pH	3.7 - 4.7	4,0 - 6,0	4.0 - 4.6	3.5 - 5.5

Preparation of Silica 3:

Silica 1 (commercially available AEROSIL® 200, Table 1) is mixed with 3 parts water and 16 parts 3-glycidyloxypropyltrimethoxysilane (commercially available e.g. from
5 Evonik Industries AG under the brand name Dynasylan® GLYMO) and the mixture is heat-treated at 140° C under inert gas. The physical and chemical properties of the obtained Silica 3 are shown in Table 1.

Example 1 - Adhesion Testing:

ASTM D 1002 and ASTM D 1151 were used to perform the testing. A bishenol-A
10 resin , EPON® 828 (Hexion Speciality Chemicals, Inc.) and amine curing agent , EPIKURE® 3055 (Hexion Speciality Chemicals, Inc.) were used as the base adhesive. Fumed Silica 3 at a 4.0 % w/w loading level , which contains epoxy groups and has been prepared by flame hydrolysis and which has a specific surface area of 145 m²/g and a carbon content of 5 % , was dispersed in both parts as well as 4.0 %
15 w/w Silica 2 (AEROSIL® R 202) and 4.0 % w/w Silica 1 (AEROSIL® 200) and a mixture by volume tested in a lap shear configuration. The substrate was aluminium alloy T6061 with an unpolished (mill) finish 3 mm thick and cut to 25 mm by 75 mm panels. The substrate was prepared by triple cleaning in ultrasonic water bath and finally dipping in an acid solution to etch the surface. Within 24 hours, lap shears
20 were assembled using a 645 mm² contact area. Adhesive was applied and a 5 mil (0.127 mm) stainless steel wire embedded in the adhesive to give a consistent bond line thickness. Three specimen were assembled and clamped together to ensure proper alignment of the substrates and allowed to cure at 63 °C (± 2 °C) for 48 hours prior to dynamic tensile testing. A second set of three specimen was prepared the
25 same way, subjected to full immersion in de-ionized water maintained at 63 °C (± 2 °C), and tested immediately after water removal. The average values are shown in Table 2.

Table 2: Adhesion Testing: Change after 1 week at 63°C water soak

	Lap shear adhesion [MPa]	Lap shear adhesion [MPa] after 1 week at 63°C water soak
Silica 1 , comparative (hydrophilic fumed silica)	8.3	4.4
Silica 2 , comparative (PDMS treated fumed silica)	12.7	6.2
Silica 3 , used according to the invention (epoxy silane treated fumed silica)	10.5	11.9

The best performing mixture was the system based on Silica 3. While the initial strength was lower than the system based on Silica 2, the one –week water soak cycle showed an increase in strength. All other systems showed a significant decrease in strength of 51 % (Silica 2) and of 47 % (Silica 1). The system based on Silica 3 showed an increase of 13 % in strength.

Conclusion:

An increase in strength in a reactive resin may be explained by a continuation in the cure mechanism, often called post-cure. This may be a result of continued reaction of residual epoxide groups of the epoxy silane treated fumed silica both with the epoxy adhesive and the substrate. It may also be due to changes in the lattice network of the epoxy resin. It is common to hold an epoxy at temperatures near the glass transition point to improve the uniformity of the lattice network. For the EPON® 828 / EPICURE® 3055 combination the glass transition temperature is 67 °C.

The system based on the mixture of Silica 3 performed the best compared to the fumed silicas 1 and 2. This new grade of treated fumed silica may be a better option for formulators seeking improved performance especially regarding improved storage stability of epoxy based structural adhesives, because absorbed moisture is a major concern for adhesive bond systems which can reduce the bond strength.

Conventional wisdom has been that a high degree of hydrophobicity is required to improve moisture intrusion into the bond line. Traditionally, this has been accomplished by using fumed silica treated with polydimethylsiloxane fluid (PDMS), for example Silica 2 (AEROSIL® R 202). However, surprisingly Silica 3 performed the best. Applications for the epoxy based structural adhesives are for example bonded joints in metals and plastics, bonded joints and seals in glass facades for hotels, bonded joints in shipbuilding, plant construction, wind energy stations, especially bonded rotor blades, and automotive constructions.

Furthermore, this new grade of treated fumed silica is also a better option for those formulators who wish to avoid silicone oil in their formulation caused by the PDMS treated fumed silicas in their formulation, which can adversely influence adhesion and levelling of the adhesive.

Example 2 Incorporation time and rheological properties

Incorporation Time:

The incorporation time is understood to be the time during incorporation using a mixer in which the fine-particle fumed silica has completely disappeared from the surface of the binder and is wetted with the binder. Depending on the batch size, dispersing unit and formulation, the incorporation time can last for up several hours and in many applications is therefore the speed-determining step of the preparation of the product.

The fumed silica is added in portions with lowest stirring of 500 rpm of the dissolver (VMA-Getzmann Dispermat® CA 20-M1, dissolver blade 5 cm diameter), and the dispersion time is measured until the fumed silica has disappeared completely from the surface of the Renlam® M1 epoxy resin and is completely wetted with the Renlam® M1 epoxy resin.

Viscosity and Thixotropic-Index:

3.85 % fumed silica is incorporated and dispersed in Renlam M1 using the vacuum-dissolver VMA-Getzmann Dispermat® CA 20-M1 at 5 min. at 3000 rpm. Viscosities
5 of the thixed Renlam® M1 epoxy resins are calculated using the Anton-Paar Physica® Rheometer MCR 301, measuring system CP25-2 at 23 °C at 5 s⁻¹ and 50 s⁻¹. Thixotropic-Indices are calculated as the quotient of the viscosity at 5 s⁻¹ divided by the viscosity at 50 s⁻¹.

Results:

10 The incorporation time in Renlam® M1 when Silica 3 (according to the invention) is used is markedly shorter than when Silica 2 (AEROSIL® R 202) or silica 4 (AEROSIL® R 805) is used. An explanation for this improved behaviour could be that the epoxy functional groups of Silica 3 are better wetted with the polar epoxy resin compared to the hydrophobic PDMS groups of Silica 2. The production of epoxy ad-
15 hesive formulations can therefore be shortened by using Silica 3 (according to the present invention). This saving in terms of time when producing the epoxy formulations enable the costs to be reduced. Furthermore, the viscosities and thixotropic indices of the epoxy resin Renlam® M1 thixed with Silica 3 (according to the present invention) are comparable with silica 4 and only slightly lower than Silica 2. Thus,
20 Silica 3 can be used as thickening agent and thixotrope in epoxy adhesives. All results are shown in Table 3.

Table 3: Incorporation time and rheological properties in epoxy resin Renlam® M1 (Huntsman Advanced Materials).

	Incorporation time [s]	Viscosity [Pa s] (shear rate: 5 s⁻¹)	Thixotropic Index
Silica 2 , comparative (PDMS treated fumed silica)	373	20.2	3.1
Silica 3 , according to the invention (epoxy silane treated fumed silica)	146	15.2	2.3
Silica 4 , comparative (octylsilane treated fumed silica)	355	15.0	2.6

Claims

1. Epoxy resin adhesive obtainable by combining an epoxy resin, 1 to 15 % by weight of surface-modified fumed silica and a curing agent, the surface-modified fumed silica bearing 3-glycidyloxypropylsilyl groups fixed on the surface and having a specific surface area (BET) of $145 \pm 20 \text{ m}^2/\text{g}$, a carbon content from about 3.5 to about 6.5 % by weight, a tapped density (measured according to DIN EN ISO 787/11) of 30 to 100 g/l, a moisture content (2 hours at 105°C) of smaller or equal to 1.0 % by weight (measured in accordance to DIN EN ISO 787/2, ASTM D 280), and a pH (in 4 % aqueous dispersion, in accordance to DIN EN ISO 787/9, ASTM D 1208) from about 4.0 to about 6.0.
2. Kit of parts comprising an epoxy resin, a curing agent and fumed silica bearing 3-glycidyloxypropylsilyl groups fixed on the surface and having a specific surface area (BET) of $145 \pm 20 \text{ m}^2/\text{g}$, a carbon content from about 3.5 to about 6.5 % by weight, a tapped density (measured according to DIN EN ISO 787/11) of 30 to 100 g/l, a moisture content (2 hours at 105°C) of smaller or equal to 1.0 % by weight (measured in accordance to DIN EN ISO 787/2, ASTM D 280), and a pH (in 4 % aqueous dispersion, in accordance to DIN EN ISO 787/9, ASTM D 1208) from about 4.0 to about 6.0.
3. Kit of parts as claimed in claim 2, wherein the fumed silica is dispersed in the epoxy resin.
4. A method for preparing the epoxy resin adhesive according to claim 1 comprising the following steps:
 - (a) mixing a hydrophilic fumed silica having a specific surface area (BET) of $200 \pm 25 \text{ m}^2/\text{g}$, a tapped density (measured according to DIN EN ISO 787/11) of 30 to 100 g/l, an average primary particle size of about 12 nm, a moisture content (2 hours at 105°C) of smaller or equal to 1.5 % by weight (measured in accordance to DIN EN ISO 787/2, ASTM D 280), and a pH (in accordance to DIN EN ISO 787/9, ASTM D 1208) from about 3.7 to about 4.7 first with water or dilute acid and then with 3-glycidyloxypropyltrimethoxysilane or 3-glycidyloxypropyltriethoxysilane or 3-glycidyloxypropyltripropoxysilane, subjecting the mixture to heat treatment

at a temperature of from 100 to 400 °C over a period from 1 to 6 hours,
(b) dispersing 1 to 15 % by weight of the fumed silica bearing 3-
glycidyloxypropylsilyl groups fixed on the surface obtained in step (a) to an
epoxy resin and
5 (c) mixing the dispersion of step (b) with a curing agent.

5. The use of fumed silica bearing 3-glycidyloxypropylsilyl groups fixed on the
surface and having a specific surface area (BET) of $145 \pm 20 \text{ m}^2/\text{g}$, a carbon
content from about 3.5 to about 6.5 % by weight, a tapped density (measured
according to DIN EN ISO 787/11) of 30 to 100 g/l, a moisture content (2 hours
10 at 105° C) of smaller or equal to 1.0 % by weight (measured in accordance to
DIN EN ISO 787/2, ASTM D 280), and a pH (in 4 % aqueous dispersion, in
accordance to DIN EN ISO 787/9, ASTM D 1208) from about 4.0 to about 6.0
for reinforcing, thickening and rendering thixotropic an epoxy resin adhesive.
6. A method for improving the storage stability and bond strength of an epoxy
15 resin adhesive under wet environmental conditions and/or after water
immersion comprising the combination of an epoxy resin, 1 to 15 % by weight
of fumed silica and a curing agent, the fumed silica bearing 3-
glycidyloxypropylsilyl groups fixed on the surface and having a specific surface
area (BET) of $145 \pm 20 \text{ m}^2/\text{g}$, a carbon content from about 3.5 to about 6.5 %
20 by weight, a tapped density (measured according to DIN EN ISO 787/11) of 30
to 100 g/l, a moisture content (2 hours at 105° C) of smaller or equal to 1.0 %
by weight (measured in accordance to DIN EN ISO 787/2, ASTM D 280), and
a pH (in 4 % aqueous dispersion, in accordance to DIN EN ISO 787/9, ASTM
D 1208) from about 4.0 to about 6.0.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/057336

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09J163/00 C08K9/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09J C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	DE 10 2006 061057 A1 (WACKER CHEMIE AG [DE]) 26 June 2008 (2008-06-26) paragraphs [0111], [0114]; example 5 -----	1-6
Y	DATABASE WPI Week 200707 Thomson Scientific, London, GB; AN 2007-064049 XP002682552, & JP 2006 328349 A (TOKUYAMA CORP) 7 December 2006 (2006-12-07) abstract ----- -/-	1-6



Further documents are listed in the continuation of Box C.



See patent family annex.

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Ellrich, Klaus

INTERNATIONAL SEARCH REPORT

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PCT/EP2013/057336

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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