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(54) Title: SILICA AND ALSO ADHESIVE AND SEALANT SYSTEMS

(57) Abstract: Hydrophilic fumed silica is structurally modified using a ball mill and, if desired, is reground. It can be used in adhesive and sealant systems.

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Silica and also adhesive and sealant systems

The invention relates to hydrophilic fumed (pyrogenically prepared) silica (silicon dioxide) and also to adhesive and sealant systems.

- 5 Fumed silica is known from Ullmann's Enzyklopädie der technischen Chemie, 4th Edition, Volume 21, page 464 (1982).

It is prepared by flame hydrolysis (pyrolysis) of vaporizable silicon halogen compounds in an oxyhydrogen
10 flame.

The dry, ball mill treatment of hydrophobic and hydrophilic fumed silicas for the purpose of modifying the structure is known (EP 0 637 616 A1).

- For instance, a hydrophilic fumed silica (Aerosil® 300)
15 having a tamped density of 25 g/l is structurally modified in a ball mill without addition of water. A tamped density of 308 g/l is achieved (page 6, line 38).

- The silica with a tamped density of 308 g/l has the disadvantage that it is difficult to incorporate into
20 polymeric systems or dispersions, such as coating materials.

Document EP 0 637 616 A1 does not describe the regrinding of structurally modified fumed silicas.

- The invention provides hydrophilic fumed silicas which are
25 characterized in that they are structurally modified.

In one embodiment of the invention the structurally modified fumed silicas of the invention may be reground.

The structurally modified, hydrophilic fumed silica of the invention can have a tamped density of 100 to 250 g/l.

Starting from a fumed hydrophilic silica having a BET surface area of $200 \pm 25 \text{ m}^2/\text{g}$, the structurally modified silica of the invention can have a DBP number of 160 to 240 g/100g (DIN 53601).

- 5 Starting from a fumed hydrophilic silica having a BET surface area of $300 \pm 30 \text{ m}^2/\text{g}$, the structurally modified silica of the invention can have a DBP number of 180 to 250.

10 The water content not only of the silica starting materials but also of the structurally modified silicas of the invention can be less than 1.5% by weight.

The reground, structurally modified silicas of the invention can have a grindometer value of less than or equal to 60 μm , preferably less than or equal to 40 μm .

- 15 The structurally modified silica of the invention can have a water content higher than that of the silica starting materials. The water content can be 3.5% by weight at maximum.

20 The invention further provides a process for preparing the hydrophilic fumed silica of the invention, which process is characterized in that hydrophilic fumed silica is structurally modified and, if desired, reground.

The structural modification is carried out by means of a ball mill or of a continuously operating ball mill.

- 25 Before and/or during the structural modification it is possible to add water to the silica. Addition of water may take place in an amount of 0.5% to 5% by weight, preferably 0.5% to 2% by weight. It produces a lower thickening effect.

30 Following structural modification, the DBP number is lower or cannot be determined.

The structural modification raises the grindometer value (grain limit). The increased grindometer value, however, is reduced again in the course of regrinding.

During the structural modification, the agglomeration
5 structure of the fumed silica is very largely destroyed. This can be seen from the figures.

Figure 1 shows the original fumed silica, while Figure 2 depicts the structurally modified fumed silica.

The structurally modified fumed silica has a higher tamped
10 density. The individual aggregates that remain are more spherical. They can have a thickening effect of < 1400 . In the case of an initial silica having a BET surface area of $200 \pm 25 \text{ m}^2/\text{g}$, the thickening effect can be < 1000 . In the case of an initial silica having a BET surface area of
15 $300 \pm 30 \text{ m}^2/\text{g}$, the thickening effect can be < 1400 .

Regrinding reduces the grindometer value, the particle size distribution being shifted towards smaller particles.

The structure of the fumed silica that remains following structural modification is not impaired by regrinding.

20 Regrinding has virtually no effect on the performance properties of the structurally modified fumed silica, since the energy input in regrinding is lower than in the ball mill.

Examples of apparatus that can be used for regrinding
25 include the following: air-jet mill, toothed-disk mill or pinned-disk mill.

Structural modification and/or regrinding may be followed by heat treatment. This heat treatment may take place batchwise, in a drying cabinet, for example, or
30 continuously, in a fluid bed or fluidized bed, for example.

As hydrophilic fumed silicas it is possible to use

hydrophilic fumed silicas which have a BET surface area of 50 ± 30 to 380 ± 30 m²/g. With particular preference it is possible to use hydrophilic fumed silicas which have a BET surface area of 200 ± 25 or 300 ± 30 m²/g.

- 5 It is possible more particularly to use the following hydrophilic fumed silicas, listed in Table 1.

5

Table 1

		AEROSIL® 200	AEROSIL® 300
CAS Reg. number			
Attitude to water			
Appearance			
BET surface area 1)	m ² /g	200 ± 25	300 ± 30
Average primary particle size	nm	12	7
Tamped density 2)	g/l	about 50	about 50
Compacted product (Coded "C")	g/l	about 120	about 120
Loss on drying 3) (2 h at 105°C) on leaving supply plant	%	< 1.5	< 1.5
Loss on ignition 4)7) (2 h at 1.000°C)	%	< 1	< 2
pH 5) (in 4% aqueous dispersion)		3.7 - 4.7	3.7 - 4.7
SiO ₂ 8)	%	> 99.8	> 99.8
Al ₂ O ₃ 8)	%	< 0.05	< 0.05
Fe ₂ O ₃ 8)	%	< 0.003	< 0.003
TiO ₂ 8)	%	< 0.03	< 0.03
HCl 8)10)	%	< 0.025	< 0.025
Sieve residue 6) (Mocker method, 45 µm)	%	< 0.05	< 0.05

1) based on DIN 66131

2) based on DIN ISO 787/XI, JIS K 5101/18 (unsieved)

3) based on DIN ISO 787/II, ASTM D 280, JIS K 5101/21

4) based on DIN 55921, ASTM D 1208, JIS K 5101/23

5) based on DIN ISO 787/IX, ASTM D 1208, JIS K 5101/24

6) based on DIN ISO 787/XVIII, JIS K 5101/20

7) based on material dried at 105°C for 2 hours

8) based on material calcined at 1000°C for 2 hours

9) special moisture-protective packaging

10) HCl content in constituent from loss on ignition

5

10

The advantages of the structurally modified and reground silicas of the invention include the following:

The structurally modified and reground silicas of the invention possess lower grindometer values, lower grit
5 values in conjunction with lower tamped densities, lower thickening effects and reduced structure (DBP values). They are easy to incorporate into the polymer systems.

The silicas of the invention can be employed in adhesive and sealant systems.

10 Adhesive and sealant systems are known from Ullmann's Enzyklopädie der technischen Chemie, 4th Edition, Volume 14, page 227 (1997).

They consist of high-polymer compounds having extremely good strength properties. The majority of adhesives and
15 sealants comprise high molecular mass organic compounds as base materials, or reactive organic compounds which are precursors of polymeric compounds and react to polymers in the course of the adhesive bonding and sealing operation.

It is known that for various adhesive and sealant systems,
20 for example those based on unsaturated polyester resins, polyurethane resins or vinyl ester resins, hydrophilic fumed silicas are very effective thixotroping agents in comparison to other silicas (Degussa Schriftenreihe Pigmente (2001) No. 27 and No. 54).

25 Disadvantageously, on account of their particle size distribution, fumed silicas frequently produce roughness of the adhesive and sealant surface, which together with a high thickening effect only allows low levels of filling.

This effect is a significant disadvantage. For this reason,
30 hydrophilic fumed silica can be used only in limited adhesives and sealants. Particularly in the context of use in gelcoats, such behaviour cannot be tolerated, since the

gelcoat later represents the face of a moulding's surface. The thickening effect only allows low levels of filling, and so the mechanical properties cannot be further increased.

- 5 It is therefore an object to produce adhesive and sealant systems in which these disadvantages, such as surface roughness and high thickening, do not occur.

The invention provides adhesive and sealant systems characterized in that they contain 0.5% to 20% by weight of
10 structurally modified hydrophilic and reground fumed silica by grinding.

The adhesive and sealant systems may have been obtained on the basis of unsaturated polyester resins, epoxy resins, polyurethane, silane-terminated polymers, vinyl ester
15 resins, acrylates, polyvinyl acetate, polyvinyl alcohol, polyvinyl ethers, ethylene-vinyl acetate, ethylene-acrylic acid copolymers, polyvinyl acetates, polystyrene, polyvinyl chloride, styrene-butadiene rubber, chloroprene rubber, nitrile rubber, butyl rubber, polysulphide, polyethylene,
20 polypropylene, fluorinated hydrocarbons, polyamides, saturated polyesters and copolyesters, phenol-formaldehyde resins, cresol-/resorcinol-formaldehyde resins, urea-formaldehyde resins, melamine-formaldehyde resins, polyimides, polybenzimidazoles or polysulphones.

- 25 One preferred subject of the invention may be a gelcoat based on unsaturated polyester resins.

Sealants may be non-metallic materials, both plastic and elastic, having adhesion properties and intended for filling joints and cavities between material unions, which
30 adhere to the sides of the material after setting, and seal the joints against ambient media. Like the adhesives, the sealants may both be physically setting systems or chemically curing (crosslinking) systems. Besides the base

polymer, sealants may comprise further constituents, such as, for example, plasticizers, solvents (ketones for example), water, fillers (chalk for example), thixotroping agents (fumed silica for example), adhesion promoters
5 (silanes for example), colour pastes (pigment-grade carbon black for example) and also further additives (for example catalysts, ageing inhibitors).

Adhesives may be non-metallic substances which are able to join adherends by two-dimensional attachment and internal
10 strength (adhesion and cohesion). Adhesives can mean products which, in accordance with their respective chemical composition and the physical state prevailing at the time of application to the adherends, allow wetting of the surfaces and, in their bonded joint, form the adhesive
15 layer needed for transmission of force between the adherends.

Like the sealants, adhesives may comprise further components as well as the base polymer, such as, for example, solvents (ketones for example), water, fillers
20 (chalk for example), thixotroping agents (fumed silica for example), adhesion promoters (silanes for example), colour pastes (pigment-grade carbon black for example) and also further additives (for example catalysts, ageing inhibitors).

25 In comparison to sealants, adhesives may have higher tensile shear strengths and lower extension values. In other words, adhesives may be hard to elastic, and sealants may be elastic to plastic.

Unsaturated polyester resins can be obtained by
30 polycondensation of unsaturated and saturated dicarboxylic or polycarboxylic acids with alcohols. Given a suitable reaction regime, the double bonds remain in the acid and/or alcohol and permit reactions with unsaturated monomers, styrene for example, in accordance with the principle of

addition polymerization.

Unsaturated dicarboxylic acids that can be used are as follows: maleic anhydride, maleic acid, fumaric acid.

Possible saturated dicarboxylic acids are as follows:

- 5 ortho-phthalic acid and ortho-phthalic anhydride, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, adipic acid, azelaic acid, sebacic acid, Het acid, tetrabromophthalic acid.

Glycols that can be used are as follows:

- 10 propylene 1,2-glycol, ethylene glycol, butylene glycol, neopentyl glycol, 2,2,4-trimethylpentane-1,3-diol, dibromoneopentyl glycol, diethylene glycol, triethylene glycol, dipropylene glycol, pentaerythritol diallyl ether, dicyclopentadiene.

- 15 Monomers for the crosslinking may be: styrene, alpha-methylstyrene, meta- and para-methylstyrene, methyl methacrylate, diallyl phthalate, triallyl cyanurate.

- This listing does not exhaust the number of possible starting materials. The skilled person will be able, depending on the raw material situation, to use other compounds as well. Furthermore, the addition of dicyclopentadiene is customary, and the reactivity of the resins is modified as a result. The "unsaturated polyester resins" produced can be used as such or in dilution with reactive monomers. Reactive monomers may be styrene, stilbene, esters of acrylic acid, esters of methacrylic acid, diallyl phthalate, and other unsaturated compounds, provided that they have a sufficiently low viscosity and adequate miscibility with the unsaturated polyester resin.
- 20
- 25

- 30 Epoxy resins can be prepared for example by condensing 2,2-bis(4-hydroxyphenyl)propane, also called bisphenol A, and epichlorohydrin in a basic medium. Depending on the equivalents of both reactants that are employed, the

products are glycidyl ethers with different molar masses. Use may also be made of epoxy resins from bisphenol F, novolak epoxy resins, and cycloaliphatic and heterocyclic epoxy resins.

- 5 Since epoxy resins on their own are poor film formers, molecular enlargement is required by means of suitable crosslinking agents. Examples of crosslinking agents that can be used for epoxy resins include polyamines, polyamino-amides, carboxylic anhydrides and dicyandiamides.
- 10 Amine curing agents that can be used include aliphatic, cycloaliphatic, aromatic and araliphatic polyamines. Curing takes place without elimination of reaction products. It generally involves the addition of a reactive hydrogen atom to the epoxide group, with formation of a hydroxyl group.
- 15 Polyurethanes, also called polyisocyanate resins, derive from isocyanic acid. As an extremely reactive compound, it undergoes addition very readily with compounds which possess an active (mobile) hydrogen atom. In the course of this reaction the double bond between the nitrogen and the
- 20 carbon is cleaved, the active hydrogen becoming attached to the nitrogen and the R₂-O group to the carbon, to form a urethane group. In order to obtain higher molecular mass crosslinked polyurethanes of the kind needed for adhesive and sealant layers, it is necessary to provide reaction
- 25 partners which are starting products having at least two functional groups, such as di- or triisocyanates, for example diphenylmethane 4,4-diisocyanate (MDI) with polymeric fractions, or reaction product of tolylene diisocyanate (TDI) and polyols, and polyhydric alcohols
- 30 (diols or polyols, compounds having two or more hydroxyl functions in the molecule). Alcohols of this kind may also be present, for example, in the form of saturated polyesters, which are prepared with an excess of polyalcohols.

Two-component reactive adhesives are composed of a low

molecular mass polyisocyanate and a likewise relatively low molecular mass polyesterpolyol, for example polyalkylene polyadipate. Following the combining of the two components, urethane groups are formed in the adhesive or in the
5 adhesive layer.

One-component reactive adhesives may be composed of a relatively high molecular mass polyisocyanate-polyurethane, which sets by reacting with atmospheric moisture. In principle the situation here as well is one of two inter-
10 reacting chemical components, but only one physical component is supplied for adhesive processing. Since, on reaction with moisture, the simple low molecular mass polyisocyanates form relatively hard and brittle adhesive layers with low strength values, the one-component systems
15 start from precrosslinked polymers, known as prepolymers. These compounds are prepared from relatively high molecular mass polyols with a stoichiometric excess of isocyanate. In this way, the compounds present already possess urethane bonds, but in addition possess reactive isocyanate groups
20 as well, which are amenable to the reaction with moisture. The reaction with water proceeds with the formation of a urea bond. The primary amines formed in the course of the decomposition reaction react immediately with further isocyanate groups to form polyureas. In the case of the
25 one-component systems, therefore, the fully cured polymer contains not only urethane compounds but also urea compounds.

Solvent-borne polyurethane adhesives are available as physically setting systems and as chemically reacting
30 systems. In the case of the physically setting systems the polymer takes the form of a high molecular mass hydroxyl polyurethane. The solvent used is, for example, methyl ethyl ketone. The chemically reacting systems include, further to the hydroxyl polyurethane, a polyisocyanate as
35 crosslinker and as a second component.

Dispersion-based adhesives comprise a high molecular mass polyurethane in dispersion in water.

In the case of thermally activable polyurethane adhesives the isocyanate component is in "capped" or "blocked" form
5 in a compound which eliminates the isocyanate component only at a relatively high temperature.

Reactive polyurethane hotmelt adhesives are prepared by using relatively high molecular mass, crystallizing and meltable diol and isocyanate components. These components
10 are applied as hotmelt adhesives at temperatures from around 70°C to 120°C to the adherends. After cooling (physically setting) the bond acquires a sufficient initial strength, which allows rapid further processing. Subsequently, as a result of additional moisture exposure
15 of the reactive isocyanate groups still present, cross-linking then takes place via urea bonds (chemical reaction), to form the adhesive layer polymer.

The term "silane-terminated polymers" or else "silane-modified polymers" embraces all of those prepolymers which,
20 either at the chain ends or pendently, carry silyl groups having at least one hydrolysable bond, but whose polymer backbone does not contain the siloxane bond $(\text{SiR}_2\text{O})_n$ typical of silicones.

In general it can be assumed that any silane-modified
25 polymer, irrespective of its chemical structure, will have the qualities of a hybrid: the curing is similar to that of the silicones, and the other properties are shaped by the various possible polymer backbones between the silyl groups. Silane-terminated or silane-modified polymers can
30 be classed in terms of their structure between the polyurethanes and the silicones.

The synthesis of the silane-modified polymers encompasses a number of stages. The initial basis is dihydric or

trihydric polyoxypropylene glycol, which is converted into the corresponding bisallyl compound. That compound is reacted to form the desired end product, bis(3-(methyl-dimethoxysilyl)propyl)polyoxypropylene.

- 5 The silyl groups introduced into the chains crosslink there via mechanisms of the kind known in silicone chemistry. That is, they react, with elimination of small amounts of water or methanol, and so give an elastic and insoluble network.
- 10 There are further possible methods of obtaining sealants and adhesives based on silicone-modified polymers, for example the reaction of NCO-terminated prepolymers with correspondingly reactive aminosilanes or mercaptosilanes to form the desired compounds. The polymer backbone may
- 15 contain all of the conceivable, rational structural elements, such as ether, ester, thioether or disulphide bridges. The converse case, in which an NH_2 -, SH -, or OH -terminated prepolymer can be reacted with an isocyanate silane, is likewise conceivable. The addition of terminal
- 20 mercapto groups (either in the prepolymer or in the silane) to C-C double bonds offers a further route of technical interest.

- On the chemical side, vinyl ester resins possess a certain relationship to the UP resins, for example as far as curing
- 25 reaction, processing technology and field of use are concerned. These resins are polyadducts of liquid epoxy resins and acrylic acid. As a result of reduction of ester groups in the molecule chain, these resins have better hydrolysis resistance in tandem with effective elasticity
- 30 and impact toughness. Monomers used for crosslinking are the same as for the unsaturated polyester resins, styrene in particular.

The collective term "acrylate-based adhesives" encompasses all of the reactive adhesives whose curing takes place via

the carbon-carbon double bond of the acrylic group.

Particular significance in adhesive formulations has been acquired by the methacrylic esters and the alpha-cyanoacrylic esters. The curing of the acrylate adhesives is accomplished by addition polymerization, in the course of which an initiator triggers a chain reaction leading to a continuous concatenation of molecules (monomers) via the carbon double bond, to give the cured adhesive. The polymerization of the "acrylate" adhesives can be initiated by means of free radicals (free-radical polymerization). The polymerization may also be initiated, moreover, in the case of the alpha-cyanoacrylates, by means of anions (anionic polymerization).

In accordance with the polymerization mechanism that is utilized for curing, the acrylate adhesives are also subdivided into the following groups:

- anionically curing adhesives: alpha-cyanoacrylate 1-component adhesives
- free-radically curing adhesives: anaerobic 1-component adhesives
- free-radically curing adhesives: 2-component adhesives

In the case of the sealants based on polyacrylic esters or acrylic ester copolymers and polymethacrylic esters a distinction is made between solvent-borne and aqueous systems. Polyacrylate sealants cure physically by evaporation of the solvent or of the dispersion water.

Polyvinyl acetate is the product of polymerization of vinyl acetate. Owing to the strongly polar acetate group present in the molecule, polyvinyl acetate possesses very good adhesion properties to many adherend surfaces. Use is predominantly as a dispersion-based adhesive with a solids content of approximately 50% to 60%, in some cases also

based on vinyl acetate copolymers (with vinyl chloride, for example).

Polyvinyl alcohol comes about as a product of hydrolysis of polyvinyl acetate and other similar polyesters. Depending
5 on molecular weight, the polyvinyl alcohol takes the form of a liquid having a more or less high viscosity. It is used, for example, for bonding cellulosic materials, such as paper, cardboard, wood and the like, and also as a protective colloid for stabilizing and increasing the
10 setting rate of dispersion-based adhesives.

Among the polyvinyl ethers, the following three polymers in particular are preferred as base materials for adhesives:

- polyvinyl methyl ethers
- polyvinyl ethyl ethers
- 15 - polyvinyl isobutyl ethers

The polyvinyl ethers at moderate degrees of polymerization are tacky plasticizing resins possessed of very good adhesion properties to porous and smooth surfaces.

Polyvinyl methyl ether is notable in particular for the
20 fact that, owing to its water of solubility, it can be moistened again and therefore, for example, as a mixture with dextrin or animal glues, used as a gum on label papers, endows them with improved adhesion. On account of their permanent tackiness, polyvinyl ethers are also
25 employed in pressure-sensitive adhesives.

Ethylene-vinyl acetates are copolymers of ethylene and vinyl acetate. In the molecular structure the vinyl acetate molecules are incorporated randomly in the ethylene chain. While the elimination of acetic acid makes the polyvinyl
30 acetate relatively unstable under temperature load, the copolymers with ethylene are significantly more resistant in terms of oxidation and thermal degradation. For this

reason, EVA copolymers (with an approximately 40% vinyl acetate fraction) are among an important group of base hotmelt adhesive materials.

Ethylene-acrylic acid copolymers are copolymers of ethylene
5 and of acrylic acid and/or acrylic esters.

These copolymers, which combine the chemical resistance of polyethylene with the good properties of the acid and/or ester moiety, represent important base polymers for hotmelt adhesives. The ester component used may preferably be ethyl
10 acrylate.

Polyvinylacetals come about through the action of aldehydes on alcohols. The most important acetals for adhesives' manufacture are

- polyvinylformal
- 15 - polyvinylbutyral.

Both serve as a plasticizing component for phenolic resin-based adhesives. Polyvinylbutyral, moreover, finds application as an adhesive film in laminated safety glass.

Polystyrene is the product of polymerization of styrene.

20 The monomer (monostyrene) is in use as a constituent for adhesive base materials predominantly in two sectors:

- as a copolymer with plasticizing monomers, particularly butadiene, for the preparation of styrene-butadiene dispersions;
- 25 - as a "polymerizable" solvent for copolymerization with unsaturated polyesters.

Polyvinyl chloride is the polymerization product of vinyl chloride.

It can be used as a base material, particularly for

plastisol adhesives, and also as a copolymer with vinyl acetate to give vinyl chloride/vinyl acetate copolymers in solvent-based adhesives, dispersion-based adhesives, heat-sealing adhesives, and as a high-frequency welding
5 assistant.

Styrene-butadiene rubber is a typical example of a thermoplastic elastomer, combining the application properties of elastomers with those of thermoplastics. The styrene-butadiene copolymer (SBS) and the styrene-isoprene
10 copolymer (SIS) are what are called triblock copolymers, constructed linearly of successive identical monomer units in individual blocks. The end blocks are polystyrene segments, while the middle block is polybutadiene (styrene-butadiene-styrene block copolymer, SBS) or else isoprene
15 (styrene-isoprene-styrene block polymer, SIS).

The proportion of styrene to butadiene (isoprene) fraction is approximately 1:3. Unlike adhesive layer polymers which owe their elastic properties to the addition of plasticizer, in this way an "internal plasticizing" is
20 achieved. A particular advantage of these rubber copolymers is their ability to form adhesive layers having good adhesion properties and high flexibility. Significant application therefore exists in situations where the adhesively bonded adherends are subject in practical use to
25 high deformation stresses, such as in footwear or with rubber/rubber or rubber/metal bonds, for example.

Chloroprene rubber (polychloroprene) comes about as a polymerization product and copolymerization product of chloroprene (2-chlorobutadiene). Besides the good adhesion
30 properties, the linear macromolecules possess a strong propensity towards crystallization, which contributes to a relatively high strength on the part of the adhesive layer. These polymers and copolymers are important base materials for contact adhesives. The double bond present within the
35 polychloroprene molecule allows additional crosslinking to

be carried out with correspondingly reactive molecule groups. Thermosetting components used for this purpose include isocyanates and phenolic resins.

5 In the case of polychloroprene latices the base polymers are dispersed in aqueous phase with the corresponding additives (tackifying resins, etc.) by means of suitable emulsifiers and/or protective colloids.

10 Nitrile rubber is a copolymer of butadiene with a fraction of approximately 20% to 40% of acrylonitrile. The high acrylonitrile fraction endows these polymers with effective plasticizer resistance, so making them highly suitable, for example, for the bonding of plasticized plastics.

Butyl rubber is a copolymer composed of a predominant fraction (< 97%) of isobutylene with isoprene (< 5%).
15 Within this linear chain molecule there exist, in the form of the long polyisobutylene segments, very high chain fractions of saturated character, at which no further crosslinking is possible. The sole crosslinkable component is the isoprene molecule, and so the overall properties of
20 the butyl rubber are determined by the fraction of the number of double bonds, predetermined by the isoprene.

The reactivity can be further influenced by incorporation of monomers containing chlorine or bromine.

Raw materials for polysulphide sealants have long been
25 known under the trade name Thiokol®. Polysulphide polymers are obtained by reacting dichloroethylformal with sodium polysulphide.

The molecular weight of the liquid polymers is between 3000 and 4000. By reaction with an oxidizing agent, manganese
30 dioxide for example, they can be converted into an ultimate rubber-elastic state.

Polyethylene is prepared as the polymerization product of

ethylene. The low molecular mass types, with melt indices in the range from 2 to 2000 g/10 min, have found use, in combination with tackifying resins and microwaxes, as hotmelt adhesives in the paper and cardboard industry.

- 5 Polypropylene is prepared as the polymerization product of propylene.

Polypropylene is in use as a base material for hotmelt adhesives with moderate strength properties, more specifically in the form of atactic polypropylene.

- 10 Polyfluoroethylene-propylene is a copolymer of tetrafluoroethylene and hexafluoropropylene and has been studied as a base material for hotmelt adhesives. The advantage of these products lies in the high long-term temperature durability.

- 15 The polyamides represent some of the most important base materials for the physically setting hotmelt adhesives. Suitable for the preparation of the polyamides are the reactions described below, which typically take place in the melt under a nitrogen atmosphere:

- polycondensation of diamines with dicarboxylic acids
- 20 - polycondensation of aminocarboxylic acids
- polycondensation from lactams
- polycondensation of diamines with dimerized fatty acids

- 25 Saturated polyesters and copolyesters come about through polycondensation from dicarboxylic acids and diols. They are an important base material for hotmelt adhesives.

- Phenol-formaldehyde resin polymers come about through a polycondensation reaction between phenol and formaldehyde. Highly crosslinked phenolic resins are formed which are
- 30 used as a base material for adhesives for - for example -

aircraft construction. Pure phenol-formaldehyde resins are generally too brittle. For this reason they are modified with thermoplastic polymers by copolymerization or cocondensation, for example with:

- 5 - polyvinylformal
- polyvinylbutyral
- elastomers, for example polychloroprene and nitrile rubber
- polyamides
- 10 - epoxy resins

Cresol-/resorcinol-formaldehyde resins:

Besides phenol as a starting monomer for formaldehyde condensations, use is also made of phenol derivatives, such as cresols and resorcinol, as co-reactants.

- 15 Urea-formaldehyde resins are prepared by reaction of nitrogen-containing organic compounds with aldehydes. For application as adhesives, urea and melamine in particular have acquired importance. With the urea-formaldehyde resins the reaction sequence takes place initially in the form of
- 20 an addition reaction in weakly acidic solution. The actual polycondensation reaction, leading to the formation of the polymeric adhesive layer, results in highly crosslinked polymers via the formation either of an ether bridge or of a methylene bridge.
- 25 Melamine-formaldehyde resins are prepared by reaction of melamine with formaldehyde to form methylol compounds. As in the case of the urea reactions, the polycondensation with these compounds too proceeds via methylene or methylene ether linkages to form high molecular mass,
- 30 highly crosslinked, hard and in some cases brittle adhesive layers.

Polyimides are used as adhesives for high temperature loads.

The preparation of industrially utilizable polyimides is accomplished by reaction of the anhydrides of tetrabasic acids, for example pyromellitic anhydride, with aromatic diamines, for example diaminodiphenyl oxide. Use as an adhesive is accomplished starting from a precondensate, in the form of solutions or films.

Polybenzimidazoles are classed as adhesives of high heat resistance. They come about through a polycondensation reaction from aromatic tetramines with dicarboxylic acid.

Polysulphones belong to the group of heat-resistant adhesives. They are obtained, for example, through a polycondensation reaction from dihydroxydiphenyl sulphone with bisphenol A.

Examples

Examples in accordance with the invention

The hydrophilic fumed silica Aerosil® 200 and the hydrophilic fumed silica Aerosil® 300 are structurally modified using a ball mill. In the course of this modification, as reported in Table 2, water is added and regrinding is carried out.

The structurally modified silicas obtained have a higher loss on drying than the initial silica.

The physicochemical data of the structurally modified hydrophilic silicas obtained are set out in Table 3.

Table 2

Designation	Oxide/ starting material	Structural modification	Parts of H ₂ O/100 parts of oxide	Regrinding*
Comparative Example 2	AEROSIL® 200	No	–	No
Comparative Example 2	AEROSIL® 300	No	–	No
Example 1	AEROSIL® 200	Yes	1.0	No
Example 2	AEROSIL® 200	Yes	1.5	No
Example 3	AEROSIL® 200	Yes	2.0	No
Example 4	AEROSIL® 200	Yes	5.0	No
Example 5	AEROSIL® 200	Yes	1.0	TD
Example 6	AEROSIL® 200	Yes	1.0	AJ
Example 7	AEROSIL® 300	Yes	1.33	No
Example 8	AEROSIL® 300	Yes	3.0	No
Example 9	AEROSIL® 300	Yes	3.0	No
Example 10	AEROSIL® 300	Yes	2.0	No
Example 11	AEROSIL® 300	Yes	1.0	No
Example 12	AEROSIL® 300	Yes	1.0	TD
Example 13	AEROSIL® 300	Yes	1.0	AJ

*: TD = Toothed-disk mill

5 AJ = Air-jet mill

Physicochemical data of the inventive and comparative silicas

Table 3

Designation	BET specific surface area [m ² /g]	Tamped density [g/l]	Loss on drying [%]	Loss on ignition [%]	pH	DBP [%]	Grindometer value [μm]	Thickening
Comparative Example 1	202	54	0.8	0.7	4.5	290	28	2890
Comparative Example 2	306	50	0.5	0.8	4.0	323	30	2955
Example 1	206	172	1.3	0.8	4.4	219	175	290
Example 2	203	184	1.8	0.8	4.5	201	-	-
Example 3	204	179	2.1	0.8	4.5	198	-	-
Example 4	202	189	4.6	1.0	4.6	186	-	-
Example 5	204	142	1.3	0.8	4.7	204	150	350
Example 6	203	31	0.9	1.0	4.5	199	30	760
Example 7	311	133	1.2	1.1	4.4	232	-	-
Example 8	309	185	2.8	1.2	5.7	197	-	-
Example 9	308	181	3.0	1.2	4.2	215	-	-
Example 10	308	144	2.0	1.0	4.3	227	-	-
Example 11	306	127	1.3	1.0	4.4	230	175	330
Example 12	306	117	1.1	1.1	4.4	230	150	310
Example 13	307	27	1.0	1.0	4.3	206	50	735

Table 3 shows, with reference to various physicochemical data, the effects of the structural modification and of the regrinding on the hydrophilic fumed silicas AEROSIL® 200 and AEROSIL® 300.

- 5 AEROSIL® 200 in the untreated state possesses a surface area of 202 m²/g. This is not affected or altered by the structural modification and the regrinding (see Comparative Example 1 and also Examples 1 to 6).

- 10 The tamped density is increased as a result of the structural modification. As a result of the subsequent regrinding, however, the tamped density is lowered again (see Examples 5 and 6).

The DBP number is lowered as a result of the structural modification. However, it remains unaffected by regrinding.

- 15 The grindometer value is increased as a result of the structural modification and returned to the original value by regrinding, if regrinding is carried out using the air-jet mill.

- 20 The thickening effect of the hydrophilic fumed silica is significantly lowered as a result of the structural modification, but increased somewhat as a result of regrinding.

Grindometer value

Principles:

- 25 The degree of dispersion determines the performance properties of the liquid thickened with Aerosil. The measurement of the grindometer value serves to assess the degree of dispersion. By the grindometer value is meant the boundary layer thickness below which the bits or aggregates
30 present become visible on the surface of the sample which has been coated out.

The sample is coated out in a groove with a scraper, the depth of the groove at one end being twice the size of the diameter of the largest Aerosil particles, and decreasing steadily down to 0 at the other end. On a scale indicating the depth of the groove, the depth value is read off, in micrometres, the value in question being that below which a relatively large number of Aerosil particles becomes visible as a result of bits or scratches on the surface of the binder system. The value read off is the grindometer value of the system present.

Apparatus and reagents:

Hegmann grindometer with a depth range of 100-0 micrometres.

Polyester resin dispersion with 2% Aerosil, prepared according to Testing Instructions 0380.

The testing instructions run as follows:

Apparatus and reagents:

Dispermat AE02-C1, VMA-Getzmann (dispersing disc, diameter 5 cm)

Plastic beaker, 350 ml, external diameter 8.4 cm plastic lid to fit

Monostyrene solution (100 g monostyrene + 0.4 g paraffin)

Palatal® P6-01, DSM composite resins

Centrifuge, Jouan GmbH

Thermal-conditioning cabinet

Procedure:

142.5 g of Palatal® are weighed out into a plastic beaker and 7.5 g of Aerosil are weighed in; subsequently the Aerosil is stirred carefully into the Palatal using the Dispermat at about 1000 min⁻¹ (any residues of Aerosil adhering to the beaker walls are brushed into the beaker with the Dispermat switched off) and then dispersed for 5 minutes at 3000 min⁻¹ (the distance of the dispersing disc

from the bottom of the beaker being approximately 1 mm); the beaker is covered during this procedure with a lid including a drilled hole.

In a further plastic beaker, 60 g of the dispersion and
5 27 g of monostyrene solution are introduced, with 63 g of Palatal® P6, and dispersion is carried out using the Dispermat at 1500 min^{-1} for 3 minutes (beaker covered).

This results in a concentration of 2% Aerosil in the final mixture, which contains 18% monostyrene.

10 In order to remove air bubbles, the plastic beaker, sealed, is centrifuged in a laboratory centrifuge at 2500 min^{-1} for 2.5 minutes. The dispersion is left standing in the covered beaker in a thermal-conditioning cabinet at 22°C for 1 hour and 50 minutes.

15 **A. Preparing a mixture of unsaturated polyester resins with silica filler**

Using the operating instructions described herein, mixtures of hydrophilic AEROSIL® grades and unsaturated polyester resins are prepared in order to characterize the
20 granularity and the thickening power of the silicas.

Formulation

98% Palatal A 410 (from BÜFA)
2% silica

205.8 g of Palatal A 410 and 4.2 g of silica are weighed
25 out into a PE beaker and the dissolver disc is fully immersed. Then the silica is homogenized (incorporated) at a speed $n1 = 1000 \text{ min}^{-1}$ with the lid closed. As soon as the silica has been fully incorporated the speed is increased to $n2 = 3000 \text{ min}^{-1}$ and dispersion is carried out for 5
30 minutes. Subsequently the mixture is deaerated in a vacuum cabinet and stored in a waterbath at 25°C for at least 90

minutes.

B. Measuring the viscosity of resins with silica filler

Resins (e.g. polyester resin, UP resin, vinyl ester resin) generally contain fillers for the purpose of improving the performance properties. Depending on the field of use, the nature and concentration of the filler used influence the rheological behaviour of the resin. A Brookfield DV III rheometer is used. Using a spatula, the mixture is homogenized in its storage vessel for 1 minute. In the course of this homogenization no bubbles ought to form. Subsequently the mixture is introduced into a 180 ml beaker until the beaker is almost full. Without delay, the measuring head of the rheometer is immersed fully into the mixture, and measurement takes place as follows:

5 rpm	value read off after	60 s
50 rpm	value read off after	30 s

The values read off are the viscosities [Pa*s] at the respective rpm.

C. Determining the grindometer value to DIN 53 203

Test apparatus

A Hegmann grindometer block is used.

Measuring procedure

The grindometer block is placed on a flat, slip-proof surface and is wiped clean immediately prior to testing. A bubble-free sample is then introduced at the deepest point of the groove in such a way that it flows off somewhat over the edge of the groove. The scraper is then held by both hands and placed, perpendicularly to the grindometer block and at right angles to its longitudinal edge, with gentle pressure, onto the low end of the groove. The sample is then coated out in the groove by slow, uniform drawing of

the scraper over the block. The granularity is read off no later than 3 seconds after the sample has been scraped.

The surface of the sample is viewed obliquely from above (at an angle of 20-30° to the surface) transversely to the groove. The block is held to the light in such a way that the surface structure of the sample is readily apparent.

The value found as granularity on the scale is the figure in micrometres below which a relatively large number of silica grains become visible as bits or scratches on the surface. Individual bits or scratches occurring randomly are not taken into account in this context.

The granularity is assessed at least twice, in each case on a newly spread dispersion.

Evaluation:

From the measured values the arithmetic mean is formed. The relationship between the grindometer value in micrometres and the FSPT units and Hegmann units, which are based on the inch system, is as follows:

$$B = 8 - 0.079 A$$

$$C = 10 - 0.098 A = 1.25 B$$

In this relationship:

A = Grindometer value in micrometres

B = Grindometer value in Hegmann units

C = Grindometer value in FSPT units

Examples: In accordance with methods A, B and C, the silicas are incorporated in the unsaturated polyester resin, and the viscosity (Table 4) and grindometer value (Table 5) are ascertained.

Table 4

Example	Silica	Spindle No.	Viscosity (mPa s)	
			5 rpm	50 rpm
14	4.2 g/2% from Example 11	4	2120	1780
15	4.2 g/2% from Example 12	4	2160	1840
16	4.2 g/2% from Example 13	4	4920	2476
17	4.2 g/2% from Example 1	4	2080	1796
18	4.2 g/2% from Example 5	4	2120	1820
19	4.2 g/2% from Example 6	4	4920	2456
20	4.2 g/2% Aerosil® 200	5	13280	4320
21	4.2 g/2% Aerosil® 300	5	13200	4480

The silicas of the invention exhibit very low thickening as compared with the comparison silicas, and so slightly higher levels of filling can be achieved (see Table 5).

Example 5

Example	Silica	Spindle No.	Viscosity (mPa s)	
			5 rpm	50 rpm
22	16g/7.2% from Example 11	6	19600	6280
23	16g/7.2% from Example 12	6	22200	6880
24	10g/4.6% from Example 13	6	22800	6200
25	16g/7.2% from Example 1	6	20400	6300
26	16g/7.2% from Example 5	6	21400	6480
27	10g/4.6% from Example 6	6	22000	6020

Table 6

Example	Silica	Grindometer value in μm
28	2% from Example 11	193
29	2% from Example 13	33
30	2% from Example 1	186
31	2% from Example 5	34
32	2% Aerosil® 200	57
33	2% Aerosil® 300	68

The silicas of the invention which have additionally been reground exhibit a very low grindometer value, which is
5 also much lower than in the case of standard materials such as AEROSIL® 200 and AEROSIL® 300.

Surprisingly, in combination with low thickening, the inventive examples exhibit significantly lower grindometer values and hence no roughnesses of the surface.

Claims

1. Hydrophilic fumed silicas characterized in that they
 are structurally modified.
2. Hydrophilic fumed silicas according to Claim 1,
5 characterized in that they are reground.
3. Process for preparing the hydrophilic fumed silicas
 according to Claim 1 or 2, characterized in that
 hydrophilic fumed silicas are structurally modified
 and, if desired, reground.
- 10 4. Process according to Claim 3, characterized in that
 the structural modification is carried out by means of
 a ball mill and water is added before and/or during
 the structural modification.
- 15 5. Adhesive and sealant systems characterized in that
 they comprise a hydrophilic fumed silica according to
 Claim 1.

The effect of structural modification in pyrogenic oxides
by reference to TEM micrographs

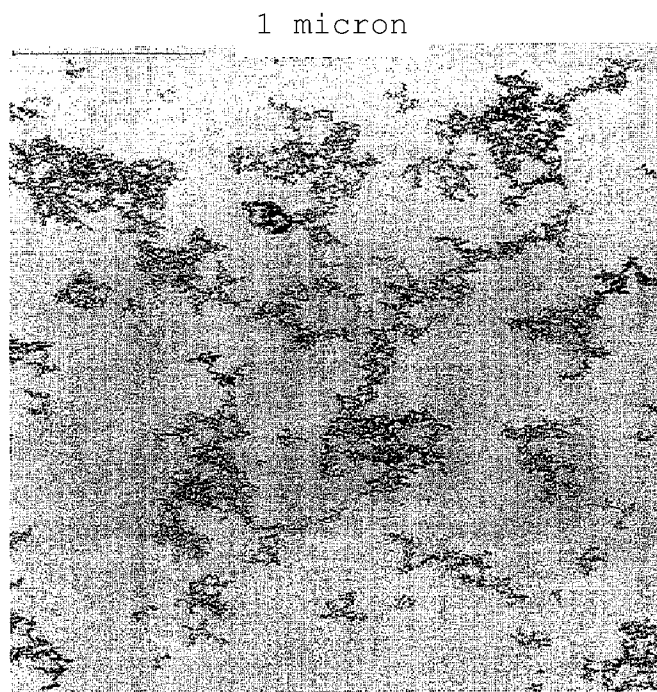


Figure 1

*Not structurally
modified*

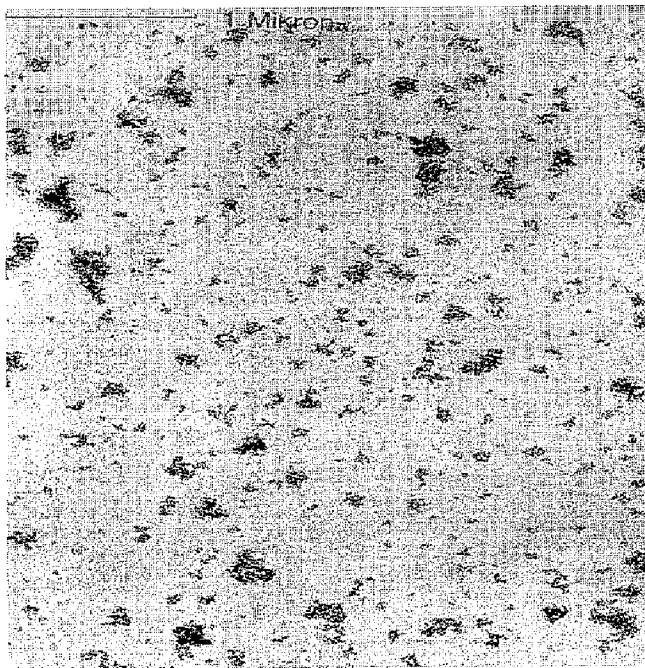


Figure 2

Structurally modified

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2008/066146

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C09C1/30 C09C3/04

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)
 C09C

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 practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 193 795 B1 (NARGIELLO MARIA R [US] ET AL) 27 February 2001 (2001-02-27) column 1, line 53 - column 2, line 8; claim 15; figures 1-3 column 3, lines 34-56 column 5, line 39 - column 6, line 15 column 7, lines 6-30	1-5
X	EP 1 801 073 A (DEGUSSA [DE]) 27 June 2007 (2007-06-27) paragraphs [0023], [0024], [0031], [0033], [0036], [0037], [0061] - [0072]; claims 1-4	1-5
X	DE 14 67 437 A1 (DEGUSSA) 19 December 1968 (1968-12-19)	1-4
A	page 4, paragraphs 1,2	5
	-/--	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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& document member of the same patent family

Date of the actual completion of the international search

20 February 2009

Date of mailing of the international search report

26/02/2009

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2008/066146

C(Continuation). . . DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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