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(54) **Title:** NANO-SILVER SEALANT COMPOSITION AND PREPARATION METHOD THEREOF

(57) **Abstract:** Disclosed herein is a nano-silver sealant composition comprising petroleum hydrocarbon as a diluent. The nano-silver sealant composition comprises 8 to 40 wt% of polydimethylsiloxane, 4 to 25 wt% of a crosslinking agent, 15 to 75 wt% of a filler, 11.99999 to 20 wt% of petroleum hy¬ drocarbon, 1 to 2 wt% of aminosilane and 0.00001 to 0.1 wt% of silver nanoparticles. Further disclosed are a nano-silver sealant using the composition and a method for preparing the nano- silver sealant. Since the nano-silver sealant shows an increased degree of dispersion of the silver nanoparticles when compared to conventional nano-silver sealants, it exhibits superior an¬ tibacterial and antifungal activity, thereby effectively preventing contamination caused by various kinds of microbes while maintaining joints in a clean state for a longer period of time.

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Description

NANO-SILVER SEALANT COMPOSITION AND PREPARATION METHOD THEREOF

Technical Field

[1] The present invention relates to a nano-silver sealant composition comprising petroleum hydrocarbon as a diluent, a nano-silver sealant using the composition, and a method for preparing the nano-silver sealant. More particularly, the present invention relates to a nano-silver sealant composition comprising 8 to 40 wt% of polydimethylsiloxane, 4 to 25 wt% of a crosslinking agent, 15 to 75 wt% of a filler, 11.99999 to 20 wt% of petroleum hydrocarbon, 1 to 2 wt% of aminosilane and 0.00001 to 0.1 wt% of silver nanoparticles, a nano-silver sealant using the composition, and a method for preparing the nano-silver sealant. Since the nano-silver sealant of the present invention shows an increased degree of dispersion of the silver nanoparticles when compared to conventional nano-silver sealants, it exhibits superior antibacterial and antifungal activity, thereby effectively preventing contamination caused by various kinds of microbes while maintaining joints in a clean state for a longer period of time.

[2]

Background Art

[3] Sealing materials are generally defined as materials which are filled to tightly seal various joints and seams against water and air. Such sealing materials are used to fix one member to another member with the aid of some extent of strength and elasticity for the purpose of improving the durability of buildings. Of these, elastic sealing materials are particularly referred to as 'sealants'. Sealants are classified into unshaped materials and shaped materials (e.g., gaskets) according to their form taken upon filling. In a narrow sense, sealing materials refer to unshaped materials. The unshaped materials are divided into two groups: sealants used in joints with an expansion/contraction allowance of ±0% or more, e.g., silicone, modified silicone, polysulfide, and polyurethane; and caulkings used in joints with an expansion/contraction allowance of ±0% or more.

[4]

Disclosure of Invention

Technical Problem

[5] Sealants are used to ensure air-tightness and water-tightness of various joints, and must satisfy basic requirements of materials capable of joining one member to another member in a waterproof manner. These basic requirements include workability (e.g.,

extrudability, non-sagging or self-levelling), curing properties (tack free time, curing rate, hardness), and attachability (cohesion failure: good adhesion, adhesion failure: bad adhesion). In addition, sealants must satisfy the following requirements: elasticity (movement resistance), which is a measure of the resistance to rupture and peeling of a completely cured film despite movement of a joint, and durability (including weather resistance, cold resistance, heat resistance, water resistance, chemical resistance), which is a measure of the resistance to loss of movement resistance in natural outdoor conditions. Thus, sealants are required to have excellent water resistance, superior attachment to members (adherends) and good adhesion irrespective of season, appropriate work time (workable time), reliable curing, good response to movements of joints, no abnormal deformation caused due to excessive stress, and strong adhesion and no deterioration for a long period of time.

[6] In addition to the above-mentioned requirements, silicone sealants must protect surface-adhered sites against contamination caused by growth of microbes and fungi after a certain time following surface adhesion. Microbes can be commonly removed through physical operations in the initial stage of contamination, but contamination accumulated for a long time is very difficult to remove, particularly deteriorating the adhesive force of the sealants. To solve the above-mentioned problems, Korean Patent Publication No. 10-0477356 (Publication date: March 22, 2005) issued to the present applicant discloses an antibacterial silicone composition comprising 20~80 wt% of polydimethylsiloxane; 5~30 wt% of methyl trimethoxy silane; 5~50 wt% of at least one filler selected from aerosol silica, quartz powder, calcium carbonate powder, precipitated silica, and diatomaceous earth; 5~30 wt% of silicone oil; 1~20 wt% of at least one antibacterial agent selected from the group consisting of silicone oil, cinnamon extract, ginger extract, herb extract, rosin, olive oil, sepiolite, porphyry, and loess; and 0.00001~0.1 wt% of silver nanoparticles wherein the silver nanoparticles are suspended in the silicone oil at 1,000~10,000 rpm, subjected to sonication, and added to the polydimethylsiloxane. The present applicant prepared a nano-silver silicone sealant using the silicone composition, and found that the nano-silver silicone sealant exhibits antibacterial and antifungal activity superior to conventional silicone sealants containing no fine silver nanoparticles. The use of the antibacterial silicone sealant by filling and joining in bathrooms, sinks, windows and other places enables effective prevention of contamination caused by various kinds of microbes and maintenance of the joints in a clean state for a longer period of time. A disadvantage of the nano-silver silicone sealant is, however, that dispersion of the silver nanoparticles is weak, leading to poor antibacterial activity and adhesion of the nano-silver silicone sealant.

[7]

Technical Solution

[8] Therefore, the present invention has been made in view of the above problems, and it is an object of the present invention to provide a nano-silver sealant using petroleum hydrocarbon as a diluent in which dispersion of silver nanoparticles is increased, thereby leading to an improvement in antibacterial, antifungal activity and adhesion of the nano-silver sealant.

[9] It is another object of the present invention to provide a nano-silver sealant composition constituting the nano-silver sealant.

[10] In accordance with one aspect of the present invention for achieving the above objects, there is provided a nano-silver sealant composition comprising 8 to 40 wt% of polydimethylsiloxane, 4 to 25 wt% of a crosslinking agent, 15 to 75 wt% of a filler, 11.99999 to 20 wt% of petroleum hydrocarbon, 1 to 2 wt% of aminosilane and 0.00001 to 0.1 wt% of silver nanoparticles wherein the crosslinking agent is selected from methyl oximino silane, vinyl oximino silane, methyl trimethoxy silane and mixtures thereof, and the filler is a one-component or multi-component type filler selected from aerosol silica, quartz powder, calcium carbonate powder, precipitated silica, diatomaceous earth and mixtures thereof.

[11] In accordance with another aspect of the present invention, there is provided a nano-silver sealant employing the nano-silver silicone composition.

[12] In accordance with yet another aspect of the present invention, there is provided a method for preparing the nano-silver sealant, the method comprising the steps of:

[13] sonicating 11.99999~20 wt% of petroleum hydrocarbon as a diluent and 0.00001~0.1 wt% of silver nanoparticles at 4,000~6,000 rpm for 1~3 hours to obtain a mixture in which the fine nanoparticles are completely dispersed (step S1);

[14] mixing the mixture of the silver nanoparticles and the petroleum hydrocarbon with 8~40 wt% of polydimethylsiloxane, and stirring the resulting mixture under vacuum for 15~50 minutes to remove air bubbles and moisture from the mixture (step S2); and

[15] adding 15~75 wt% of a filler selected from aerosol silica, quartz powder, calcium carbonate powder, precipitated silica, diatomaceous earth and mixtures thereof, 4~25 wt% of a crosslinking agent selected from methyl oximino silane, vinyl oximino silane, methyl trimethoxy silane and mixtures thereof, and 1~2 wt% of aminosilane, to the mixture obtained in step S2, followed by stirring for 15~50 minutes in the presence of a catalyst (step S3).

[16] Dibutyltin dilaurate is used as the catalyst.

[17] Vigorous stirring is required to uniformly disperse the fine silver nanoparticles in the diluent. Depending on the shape of a blade and the viscosity of the diluent, the stirring is conducted at about 1,000~100,000 rpm for one hour. After stirring, the silver

nanoparticles are uniformly dispersed in the diluent by sonication.

[18] The diluent in which the silver nanoparticles are uniformly dispersed is mixed with the organic polysiloxane, and then the crosslinking agent, the curing catalyst and the filler are added thereto to prepare a condensation-type antibacterial silicone sealant composition.

[19] Since most silicone sealants contain a certain amount of a diluent, antibacterial activity can be imparted to addition-type silicone sealants as well as condensation-type silicone sealants using the method of the present invention, by which fine silver nanoparticles are dispersed in the diluent.

[20] The fine silver nanoparticles have an average diameter ranging from 1 nm to 500 nm. The performance of the silicone sealants varies depending on the diameter of the silver nanoparticles. That is, when the fine silver nanoparticles have a diameter of 500nm or more, the antibacterial activity is poor. Meanwhile, the price of fine silver nanoparticles having a diameter smaller than 10nm is high, making it difficult to use in general-purpose sealants. Taking the cost performance of silver nanoparticles into consideration, silver nanoparticles having a diameter of from about 10 nm to about 200 nm were used in the composition of the present invention.

[21] The antibacterial activity of the fine silver nanoparticles is superior to that of com mon metal ions and zeolite-supported silver ions. This is because the antibacterial activity of silver particles has a different mechanism from that of silver ions. According to the most general theory that has hitherto been known, fine silver nanoparticles inactivate enzymes involving in the metabolism (digestion and respiration) of microbes and show complementary electrostatic interactions, leading to superior antibacterial activity. Particularly, the electrostatic properties of fine particles are unachievable by zeolite-supported silver ions.

[22] In addition, extremely small portions of silver ions supported on zeolite are substantially exposed to the outside. In contrast, silver nanoparticles are completely exposed to the outside. Therefore, the antibacterial activity of fine silver nanoparticles is tens to thousands of times greater than that of zeolite-supported silver ions, when used in the As apparent from the above description, the nano-silver silicone sealant containing silver nanoparticles according to the present invention exhibits superior antibacterial and antifungal activity to conventional silicone sealants containing no fine silver nanoparticles.

Advantageous Effects

[23] As apparent from the above description, the nano-silver silicone sealant containing silver nanoparticles according to the present invention exhibits superior antibacterial and antifungal activity to conventional silicone sealants containing no fine silver

nanoparticles.

[24]

Best Mode for Carrying Out the Invention

[25] The present invention will now be described in more detail with reference to the following examples.

[26]

[27] Nano-silver sealant compositions using petroleum hydrocarbon as diluent

[28]

[29] Example 1:

[30] A nano-silver sealant composition was prepared from 33 wt% of polydimethylsiloxane, 4 wt% of methyl oximino silane, 1 wt% of vinyl oximino silane, 5 wt% of aerosol silica, 12 wt% of petroleum hydrocarbon, 43.99999 wt% of calcium carbonate ($CaCO_3$) powder, 1 wt% of aminosilane, and 0.00001 wt% of silver nanoparticles.

[31]

Mode for the Invention

[32] Example 2:

[33] A nano-silver sealant composition was prepared from 30 wt% of polydimethylsiloxane, 5 wt% of methyl oximino silane, 4 wt% of methyl trimethoxy silane, 5 wt% of aerosol silica, 19.99999 wt% of petroleum hydrocarbon, 35 wt% of calcium carbonate ($CaCO_3$) powder, 1 wt% of aminosilane, and 0.00001 wt% of silver nanoparticles.

[34]

[35] Example 3:

[36] A nano-silver sealant composition was prepared from 40 wt% of polydimethylsiloxane, 4 wt% of methyl oximino silane, 20 wt% of petroleum hydrocarbon, 34.99999 wt% of calcium carbonate ($CaCO_3$) powder, 1 wt% of aminosilane, and 0.00001 wt% of silver nanoparticles.

[37]

[38] Example 4:

[39] A nano-silver sealant composition was prepared from 30 wt% of polydimethylsiloxane, 3.9 wt% of vinyl oximino silane, 45 wt% of aerosol silica, 20 wt% of petroleum hydrocarbon, 1 wt% of aminosilane, and 0.1 wt% of silver nanoparticles.

[40]

[41] Example 5:

[42] A nano-silver sealant composition was prepared from 33 wt% of polydimethylsiloxane, 4.9 wt% of methyl trimethoxy silane, 5 wt% of precipitated silica,

12 wt% of petroleum hydrocarbon, 44 wt% of calcium carbonate ($CaCO_3$) powder, 1 wt% of aminosilane, and 0.1 wt% of silver nanoparticles.

[43]

[44] Example 6: Preparation of sealant samples containing various amounts of silver nanoparticles

[45] Mixtures of petroleum hydrocarbon and silver nanoparticles were prepared in accordance with the compositions indicated in Table 1. Each of the mixtures of the silicone oil and the nano-silver was stirred at 5,000 rpm for one hour and then sonicated for one hour to prepare mixtures in which the fine particles were completely dispersed.

[46]

[47] Table 1

[48]

[49] Each of the petroleum hydrocarbon/nano-silver mixtures (A-N) shown in Table 1 was mixed with 40g of polydimethylsiloxane and stirred for 30 minutes. The resulting mixture was stirred under vacuum to remove air bubbles and moisture from the mixture. Dry nitrogen gas was introduced, instead of air, to release the vacuum. To the mixture were added a filler mixture of silica (25g) and porphyry (15g), 8.8g of methyl trimethoxy silane as a crosslinking agent, 1g of aminosilane, and 0.2g of dibutyltin dilaurate as a catalyst, followed by stirring for 30 minutes, to prepare a silicone sealant.

[50] Table 2 below shows the content of fine silver nanoparticles in respective silicone sealants (A-N).

[51]

[52] Table 2

[53]

[54] Example 7: Test for antifungal activity according to content of silver nanoparticles

[55] Each of the silicone sealants prepared in Example 6 was cut into specimens having dimensions of 5 cm (diameter) x 2 mm (thickness). Ten specimens per sample were tested in accordance with the KS A0702 fungal resistance test method. The test results were obtained by measuring propagation areas of fungi in the 10 specimens, averaged, and scored based on the following criteria:

[56] 5: fungi propagated in less than 10% of the total area of the specimens;

[57] 4: fungi propagated in 10-20% of the total area of the specimens;

[58] 3: fungi propagated in 20-30% of the total area of the specimens;

[59] 2: fungi propagated in 30-40% of the total area of the specimens;

[60] 1: fungi propagated in 40-50% of the total area of the specimens;

[61] 0: fungi propagated in more than 50% of the total area of the specimens.

[62]

[63] Table 3

[64] Results of antifungal activity test

[65]

[66] Example 8: Antibacterial activity test according to the content of silver nanoparticles

[67] Ten specimens were produced from each of the sealants prepared in Example 6, and antibacterial activity test was conducted in accordance with the KS K0692 agar plating method. The results are shown in Table 4 below.

[68]

[69] Table 4

[70]

Industrial Applicability

[71] Therefore, the use of the antibacterial silicone sealant by filling and joining in bathrooms, sinks, windows and other places enables effective prevention of contamination caused by various kinds of microbes and maintenance of the joints in a clean state for a longer period of time.

[72]

Claims

[1] A nano-silver sealant composition, comprising:
8 to 40 wt% of polydimethylsiloxane;
4 to 25 wt% of a crosslinking agent;
15 to 75 wt% of a filler;
11.99999 to 20 wt% of petroleum hydrocarbon as a diluent;
1 to 2 wt% of aminosilane; and 0.00001 to 0.1 wt% of silver nanoparticles.

[2] The nano-silver sealant composition according to claim 1, wherein the crosslinking agent is methyl oximino silane, vinyl oximino silane, methyl trimethoxy silane, or a mixture thereof.

[3] The nano-silver sealant composition according to claim 1, wherein the filler is aerosol silica, quartz powder, calcium carbonate powder, precipitated silica, diatomaceous earth, or a mixture thereof.

[4] A method for preparing a nano-silver sealant, comprising the steps of:
sonicating 11.99999~20 wt% of petroleum hydrocarbon as a diluent and 0.00001~0.1 wt% of silver nanoparticles at 4,000~6,000 rpm for 1~3 hours to obtain a mixture in which the fine nanoparticles are completely dispersed (step S1);
mixing the mixture of the silver nanoparticles and the petroleum hydrocarbon with 8~40 wt% of polydimethylsiloxane, and stirring the resulting mixture under vacuum for 15~50 minutes to remove air bubbles and moisture from the mixture (step S2); and
adding 15~75 wt% of a filler selected from aerosol silica, quartz powder, calcium carbonate powder, precipitated silica, diatomaceous earth and mixtures thereof, 4~25 wt% of a crosslinking agent selected from methyl oximino silane, vinyl oximino silane, methyl trimethoxy silane and mixtures thereof, and 1 wt% of aminosilane, to the mixture obtained in step S2, followed by stirring for 15~50 minutes in the presence of a catalyst (step S3).

[5] A nano-silver sealant using petroleum hydrocarbon as a diluent prepared by the method according to claim 4.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

B82B 3/00(2006.01)i

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)
IPC 8 B82B, B22F, C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
KR.JP : classes as above

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

C. 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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A	US 6,534,581 B1, (Dow Corning Corporation), 18 March 2003 (18.03.2003) see the abstract and claims.	1-5
A	US 6,416,847 B1, (09.07.2002), 09. July 2002 (09.07.2002) see the whole document.	1-5

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

* Special categories of cited documents:
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