(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
15 June 2023 (15.06.2023)

WIPO | PCT

(10) International Publication Number
WO 2023/104224 A1

(51) International Patent Classification:
C08G 77/04 (2006.01) *C09D 5/16* (2006.01)
C08K 3/08 (2006.01) *C09D 7/40* (2018.01)
C08K 3/20 (2006.01) *C09D 183/04* (2006.01)
C08K 3/22 (2006.01)

(21) International Application Number:
PCT/CZ2022/050093

(22) International Filing Date:
16 September 2022 (16.09.2022)

(25) Filing Language: Czech

(26) Publication Language: English

(30) Priority Data:
PV 2021-558 09 December 2021 (09.12.2021) CZ

(71) Applicant: **TECHNICKA UNIVERZITA V LIBERCI** [CZ/CZ]; Studentska 1402/2, 460 01 Liberec 1 (CZ).

(72) Inventors: **RUZEK, Vojtech**; Selska 600, 460 01 Liberec (CZ). **LOUDA, Petr**; 463 12 Dlouhy Most 318 (CZ). **BUCZKOWSKA, Katarzyna Ewa**; Dlazdena 1423, 463 11 Liberec (CZ).

(74) Agent: **DOBROSLAV MUSIL A PARTNERI S.R.O.**; Zabrdovicka 11, 615 00 Brno (CZ).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

WO 2023/104224 A1

(54) Title: ANTIMICROBIAL HYDROPHOBIZING LIQUID FOR SURFACE TREATMENT/PROTECTION OF SMOOTH NON-ABSORBENT MATERIALS CONTAINING METHYL SILICONE RESIN

(57) Abstract: The invention relates to an antimicrobial hydrophobizing liquid for surface treatment/protection of smooth non-absorbent materials containing methyl silicone resin dissolved in xylene. The proportion of methyl silicone resin is in the range of 15 to 70 % by weight in the solution, which further contains nanoparticles and/or microparticles of metals and/or their oxides with antimicrobial properties in an amount of 0.001 to 8 % by weight based on the total weight of the solution pro nanoparticles and in an amount of 0.1 to 8 % by weight based on the total weight of the solution for microparticles, wherein the size of the nanoparticles is in the range of 5 to 1000 nm and the size of the microparticles is in the range of 1 to 50 pm.

Antimicrobial hydrophobizing liquid for surface treatment/protection of smooth non-absorbent materials containing methyl silicone resin

Technical field

The invention relates to an antimicrobial hydrophobizing liquid for surface treatment/protection of smooth non-absorbent materials containing methyl silicone resin dissolved in xylene.

Background art

Non-absorbent materials with a smooth surface are generally at less risk from exposure to moisture than absorbent materials. There is only a danger if the surface is not hydrophobic and the liquid can remain on it, which allows it to contribute to destructive processes, especially corrosion in the case of metals or microbial degradation in the case of other materials during which certain micro-organisms can form corrosive compounds, for example, sulfur-oxidizing bacteria can produce biogenic sulfate or sulfuric acid, or fungi and lichens can mechanically erode the surface, to which contributes, among other things, long-term moisture on the surface of materials.

The usual method of protecting materials against corrosion and other destructive phenomena is using a variety of varnishes, coatings or paints which create a layer on the surface of the material and thereby prevent its contact with the external environment, although their properties differ depending on the application. Their properties can also be modified by additives. For example, the addition of metal microparticles or nanoparticles improves the antibacterial properties of the particular coating.

CZ PV 2015-417 discloses a hydrophobizing impregnation liquid with nano-additives for improving the hydrophobic and other useful properties of surfaces, which consists of an aqueous emulsion of methyl silicone resin with a minimum silicone content of 15 % by weight, containing 0.1 to 60 % by weight of a thickening agent in the form of lanolin and/or cetyl alcohol and nanoparticles of zirconium oxide $Zr0_2$ in powder form and/or nanoparticles of silicon dioxide SiO_2

in powder form and/or nanoparticles of titanium dioxide TiO_2 in powder form and/or nanoparticles of aluminium oxide Al_2O_3 in powder form at a concentration of 0. 01 to 10.0 g/l of the starting aqueous methyl silicone emulsion, wherein the nanoparticles of each oxide used in powder form have a size range of 5 nm to 100 nm and may be used either alone or in combination. The hydrophobic surface treatment will reduce the water absorption of the treated materials, increasing the durability and functionality of the products.

An alternative to varnishes and coatings can be, for example, the application of thin layers of materials with higher chemical resistance, antimicrobial properties or other advantages in comparison with the basic material. An example can be chemical nickel plating or nickel electroplating or applying a thin film by means of plasma-based methods.

The immense importance of antimicrobial treatments which prevent contamination of surfaces by dangerous microorganisms, including bacteria, moulds and viruses, is also becoming apparent nowadays. One of the ways of howto ensure antimicrobial properties is to apply layers of certain metals, especially silver, whose antimicrobial properties are the strongest of metals, or their oxides, or their nanoparticles or microparticles, which ensure antimicrobiality by disrupting the electrostatic potential of cell membranes, by formation of reactive forms of oxygen, such as free radicals or hydrogen peroxide and can also directly damage DNA or cause destructive mutations in these microorganisms.

The object of the invention is to provide hydrophobizing liquid with antimicrobial effects for surface treatment/protection of smooth non-absorbent materials.

Summary of invention

The object of the invention is achieved by a hydrophobizing liquid with antimicrobial effects for surface treatment/protection of non-absorbent surfaces of materials according to the invention, whose principle consists in that the proportion of methyl silicone resin is in the range of 15 to 70 % by weight in the solution which also contains nanoparticles and/or microparticles of metals and/or

their oxides with antimicrobial properties in an amount of 0.001 to 8 % by weight based on the total weight of the solution for nanoparticles and in an amount of 0.1 to 8 % by weight based on the total weight of the solution for microparticles, wherein the size of the nanoparticles is in the range of 5 to 1000 nm and the size of the microparticles is in the range of 1 to 50 μm.

Metals and/or their oxides with antimicrobial properties are selected from the group consisting of silver, copper, nickel, zinc, titanium, iron, copper oxide, zinc oxide, titanium dioxide, wherein they can be used either alone or in combination.

Nanoparticles and/or microparticles of the above-mentioned metals and/or their oxides with antimicrobial properties are in powder form.

Nanoparticles of the above-mentioned metals and/or their oxides with antimicrobial properties may be in the form of a colloidal solution.

By adding up to 50 % by weight of water, an aqueous emulsion is formed.

The antimicrobial hydrophobizing liquid may further comprise 0.1 to 60 % by weight of thickening agents, which in a preferred embodiment are formed by cetyl alcohol and/or lanolin.

To improve the tribological properties of the coating, the antimicrobial hydrophobizing liquid contains the addition of hydrocarbons with a C_6–C_{14} content at a concentration of 0.1- 10 ml/l of the starting solution of methyl silicone resin in xylene or the starting aqueous methyl silicone emulsion, the hydrocarbons being added either alone, or in mutual combination.

To achieve further improvement in the useful properties of the coating, the antimicrobial hydrophobizing liquid contains the addition of ethyl acetate solution in an amount of 0.1 to 60 % by weight of the starting solution of methyl silicone resin or the starting aqueous methyl silicone emulsion.

Examples of embodiment

The antimicrobial hydrophobizing liquid according to the invention is based on methyl silicone resin dissolved in xylene and, if necessary, thickened with conventional thickening agents, for example with cetyl alcohol or lanolin.

Nanoparticles and/or microparticles of at least one of metals with antimicrobial properties, such as silver, copper, nickel, zinc, titanium, iron and/or their oxides, such as copper oxide, zinc oxide, titanium dioxide, are added to this solution, wherein mutual combinations of the nanoparticles and/or microparticles of these metals and/or their oxides are also possible. An aqueous emulsion can be formed by adding water to a solution of methyl silicone resin in xylene.

The antimicrobial hydrophobizing liquid contains a solution of methyl silicone resin dissolved in xylene, with 15 to 70 % by weight of methyl silicone resin in a thickened solution (resin + xylene + thickening agents) or in an unthickened solution. The xylene solution of this resin can be used alone as a hydrophobizing coating, however, in order to add nanoparticles and/or microparticles to the powder, it is advisable to thicken it with cetyl alcohol or lanolin, to limit the sedimentation of nanoparticles and/or microparticles with a content of up to 60 % by weight of a thickening agent.

The nanoparticles and/or microparticles of metals and/or their oxides with antimicrobial properties are added to the solution in powder form in an amount of 0.001 to 8 % by weight based on the total weight of the solution for nanoparticles and in an amount of 0.1 to 8 % by weight based on the total weight of the solution for microparticles, whereupon they are thoroughly mixed to ensure that they are evenly dispersed in the solution. This applies to both the unconcentrated and concentrated solution. The mixing method is arbitrary, except for ferromagnetic metals, especially iron and nickel, where magnetic stirrers are not suitable.

The particle size of metals and/or their oxides with antimicrobial properties ranges from 5 to 1000 nm for nanoparticles and from 1 to 50 μm for microparticles.

After the application of the antimicrobial hydrophobizing liquid to the surface of the treated component, the liquid is able to harden even at normal room temperature. To achieve faster curing, a heat treatment may be carried out, namely by at least drying it at a temperature of at least 50 °C for at least 20 minutes. It is also possible to use firing at higher temperatures if the surfaces of thermally stable materials are being treated.

In the case of preparing an aqueous emulsion of a solution of methyl silicone resin in xylene, water is added for emulsification in an amount of up to 50 % by weight based on the total weight of the resulting emulsion. This procedure also enables an alternative method to deliver nanoparticles into the resulting liquid, when instead of powdered nanoparticles, an aqueous solution of nanoparticles, a so-called colloidal solution of antimicrobial metals or their oxides, as well as their mutual combination, is used. The nanoparticle size again ranges from 5 to 1000 nm and their concentration in an aqueous solution ranges from 0.01 to 20 g/l. The resulting emulsion must be homogenized. The nanoparticles and microparticles further stabilize the emulsion, and emulsification prevents their sedimentation.

The liquids with microparticles, both emulsions and simple solutions, can be mixed (homogenized) again before use, especially if sedimentation of microparticles occurs.

A mixture of C_6 to C_{14} hydrocarbons (hexane, heptane, octane, nonane, decane, undecane, dodecane, tridecane and tetradecane) may also be added to the mixture to further improve the water-repellent properties of the resulting liquid.

It is also possible to add to the mixture a solution of ethyl acetate in an amount of 0.1 – 60 % by weight based on the weight of the original solution of methyl silicone resin in xylene or the weight of the aqueous methyl silicone emulsion, for improving the useful properties of the resulting liquid.

Microparticles, nanoparticles, hydrocarbons, as well as ethyl acetate can be used alone or in mutual combination.

To verify the feasibility of the composition and properties of the antimicrobial hydrophobizing liquid according to the invention, the below specific examples of liquids according to the invention were implemented, which serve to clarify the invention, not to limit it.

Example 1

To the solution of methyl silicone resin in xylene with a mass concentration of methyl silicone resin of 50 % by weight, copper microparticles with a particle

size of up to 10 μm in size with a proportion of 5 % by weight based on the solution of methyl silicone resin in xylene. Subsequently, the solution was thoroughly mixed to ensure uniform dispersion of the particles in the solution.

The liquid thus prepared must be mixed thoroughly before use, as the microparticles sediment quickly, but their significant aggregation does not occur.

Suitable methods of application of this antimicrobial hydrophobizing liquid are coating or spraying, wherein it is suitable to use it for applications where abrasion is not expected, nor are expected other risks of mechanical damage due to the worse tribological properties of the given microparticles and where equipment is available to mix the liquid before use, whether continuously or once just before use.

Example 2

To the solution of methyl silicone resin in xylene according to Example 1, 5 % by weight of cetyl alcohol and lanolin were added in a 1/1 ratio relative to the stock solution of methyl silicone resin and 2 % by weight of copper microparticles up to 10 μm in size relative to the stock solution of methyl silicone resin in xylene. The solution was mixed thoroughly to ensure uniform dispersion of the microparticles in the solution.

Even the liquid prepared in this manner should be thoroughly mixed before use, even though in this example the sedimentation of microparticles is slower than in example 1.

The application can be carried out by spraying or coating, the liquid being usable for applications where abrasion or other risks of mechanical damage due to the inferior tribological properties of the microparticles are not expected and where equipment is available to mix the liquid before use, either continuously or once just before utilization.

Example 3

An antimicrobial hydrophobizing liquid is formed from a solution of methyl silicone resin in xylene with a proportion of 50 % by weight and a colloidal silver

solution in which the silver particle sizes range from 5 to 100 nm, with a mass concentration of silver of 50 mg/l. The proportion of the aqueous colloidal solution in the total weight of the liquid was 10 % by weight, the proportion of methyl silicone resin in the resulting solution was therefore 45 % by weight. The emulsion is subsequently homogenized.

The nanoparticles do not sediment in the thus prepared liquid and the coating or spray has a higher abrasion resistance and is therefore suitable for applications where this resistance is needed.

Example 4

An antimicrobial hydrophobizing liquid is formed from a solution of methyl silicone resin in xylene with a proportion of 50 % by weight and water, the proportion of which je 10 % by weight. The proportion of methyl silicone resin in the emulsion obtained is 45 % by weight. Subsequently, the liquid is homogenized and 5 % by weight of a thickening agent is added to it. Next, the liquid is modified by the addition of 1 % by weight of silver microparticles up to 20 μm in size and by the addition of hydrocarbons with a C_6 to C_{14} content at a concentration of 1 ml/l of the aqueous emulsion of methyl silicone resin. Then the emulsion is homogenized.

The addition of hydrocarbons serves to improve the tribological properties of the coating or spray, and silver nanoparticles are highly antimicrobial. The liquid prepared in this manner is suitable, for example, for applications with high requirements for resistance to microbial contamination.

Example 5

An antimicrobial hydrophobizing liquid is formed from a solution of methyl silicone resin in xylene with a proportion of 50 % by weight and water the proportion of which is 10 % by weight. The proportion of methyl silicone resin in the emulsion obtained is 45 % by weight. Subsequently, the liquid is homogenized and 3 % by weight of a thickening agent is added to it. Next, the liquid is modified by adding 0.1 % by weight of silver nanoparticles up to 100 μm in size. To the thus obtained aqueous emulsion, a solution of ethyl acetate is also

added in an amount of 50 % by weight of the aqueous emulsion and the emulsion is homogenized.

Silver nanoparticles exhibit antimicrobial properties even at a minimum concentration and ethyl acetate is used to improve the useful properties of the coating or spray. The liquid prepared in this manner is therefore again suitable for applications with higher requirements for antimicrobial properties.

Industrial applicability

The antimicrobial hydrophobizing liquid according to the invention is intended for the treatment of non-porous materials with a smooth surface, ensuring their hydrophobicity and antimicrobial properties, wherein these properties are achieved even when dried at room temperature. By drying at an elevated temperature, a significantly faster drying time and a slight improvement in surface hydrophobicity can be achieved.

PATENT CLAIMS

1. An antimicrobial hydrophobizing liquid for surface treatment/protection of smooth non-absorbent materials containing methyl silicone resin dissolved in xylene, **characterized in that** the proportion of methyl silicone resin is in the range of 15 to 70 % by weight in the solution which further contains nanoparticles and/or microparticles of metals and/or their oxides with antimicrobial properties in an amount of 0.001 to 8 % by weight based on the total weight of the solution for nanoparticles and in an amount of 0.1 to 8 % by weight based on the total weight of the solution for microparticles, wherein the size of the nanoparticles is in the range of 5 to 1000 nm and the size of the microparticles is in the range of 1 to 50 μm.

2. The antimicrobial hydrophobizing liquid according to claim 1, **characterized in that** the metals and/or their oxides with antimicrobial properties are selected from the group consisting of silver, copper, nickel, zinc, titanium, iron, copper oxide, zinc oxide, titanium dioxide, either alone or in combination.

3. The antimicrobial hydrophobizing liquid according to claim 2, **characterized in that** the nanoparticles and/or microparticles of metals and/or their oxides with antimicrobial properties are in powder form.

4. The antimicrobial hydrophobizing liquid according to claim 2, **characterized in that** the nanoparticles of metals and/or their oxides with antimicrobial properties are in the form of a colloidal solution.

5. The antimicrobial hydrophobizing liquid according to any of claims 1 to 4, **characterized in that** it further contains up to 50 % by weight of water, thereby forming an aqueous emulsion.

6. The antimicrobial hydrophobizing liquid according to any of claims 1 to 5, **characterized in that** it further contains 0.1 to 60 % by weight of a thickening agent.

7. The antimicrobial hydrophobizing liquid according to claim 6, **characterized in that** the thickening agent consists of cetyl alcohol and/or lanolin.

8. The antimicrobial hydrophobizing liquid according to any of claims 1 to 7, **characterized in that** it further contains hydrocarbons with a C_6 - C_{14} content at a concentration of 0.1 - 10 ml/l of the starting solution of methyl silicone resin in xylene or of the starting aqueous methyl silicone emulsion, **either alone, or in mutual combination.**

9. The antimicrobial hydrophobizing liquid according to any of claims 1 to 7, **characterized in that** it further contains an ethyl acetate solution in an amount of 0.1 to 60 % by weight based on the weight of the starting solution of methyl silicone resin or of the starting aqueous methyl silicone emulsion.

INTERNATIONAL SEARCH REPORT

International application No
PCT/CZ2022/050093

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G77/04 C08K3/08 C08K3/20 C08K3/22 C09D5/16
C09D7/40 C09D183/04
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)
C09D C08G C08K C08L C03C C09G

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 1 512 728 A1 (TOTO LTD [JP]; JHCC LTD [JP]) 9 March 2005 (2005-03-09)	6,7
A	page 4, paragraph 30 page 5, paragraph 36-39 and 43-45 page 6, paragraph 56-58 page 7, paragraph 67 and 71 page 8, paragraph 77 page 15, paragraph 113-114 page 16, paragraph 123-124 examples 7 and 9-11; table 4	1-5,8,9

X	CN 109 206 746 A (LU BINGKUN) 15 January 2019 (2019-01-15)	1-5,8,9
Y	abstract	6,7

	-/--	

[x] Further documents are listed in the continuation of Box C.
[x] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 January 2023	02/02/2023

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Denis, Cécile

2

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/CZ2022/050093

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2009/045302 A2 (NDSU RES FOUNDATION [US]; CHISOLM BRET J [US]; MAJUMDAR PARTHA [US]) 9 April 2009 (2009-04-09) page 2, paragraph 5 - page 3, paragraph 8 page 8, paragraph 24 page 9, paragraph 26	1-9
A	US 2019/210007 A1 (FURUDATE MANABU [JP] ET AL) 11 July 2019 (2019-07-11) page 1, paragraph 16-19 page 2, paragraph 31-33 page 4, paragraph 69-70; examples Preparation example 1-3	1-9
A	US 2005/227859 A1 (NAKABAYASHI AKIRA [JP] ET AL) 13 October 2005 (2005-10-13) page 3, paragraph 26-28 page 8, paragraph 137-138; example 1	1-9

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/CZ2022/050093

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1512728 A1	09-03-2005	AU 2003241999 A1	19-12-2003
		CN 1656183 A	17-08-2005
		DK 2316895 T3	26-08-2013
		EP 1512728 A1	09-03-2005
		EP 2316895 A1	04-05-2011
		ES 2425840 T3	17-10-2013
		HK 1079231 A1	31-03-2006
		KR 20050013560 A	04-02-2005
		KR 20100063809 A	11-06-2010
		US 2005277543 A1	15-12-2005
		US 2009226620 A1	10-09-2009
		WO 03102091 A1	11-12-2003
CN 109206746 A	15-01-2019	NONE	
WO 2009045302 A2	09-04-2009	NONE	
US 2019210007 A1	11-07-2019	AU 2017320240 A1	17-01-2019
		CN 109641430 A	16-04-2019
		EP 3505343 A1	03-07-2019
		JP 6579274 B2	25-09-2019
		JP WO2018042804 A1	14-03-2019
		KR 20190049695 A	09-05-2019
		TW 201815573 A	01-05-2018
		US 2019210007 A1	11-07-2019
		WO 2018042804 A1	08-03-2018
US 2005227859 A1	13-10-2005	AU 2002306213 A1	19-12-2003
		CN 1638868 A	13-07-2005
		EP 1518601 A1	30-03-2005
		JP 4282597 B2	24-06-2009
		JP WO2003101615 A1	29-09-2005
		KR 20050013564 A	04-02-2005
		US 2005227859 A1	13-10-2005
		WO 03101615 A1	11-12-2003