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Description

As prior art in the field of strengthening, by means of a base coating, the adhesion of organopolysiloxane elastomers to supports on which the elastomers have been produced, the joints thus obtained being exposed to the action of water, there is mentioned US 4 133 938 (issued 9th January 1979, Th. G. Bingham, SWS Silicones Corporation).

The subject of the invention is a process for strengthening the adhesion of organopolysiloxane elastomers, produced from compositions that can be cross-linked at room temperature, to supports, by applying a base coating to the support before applying the composition that can be cross-linked to form the elastomer, this composition containing, in addition to cross-linkable diorganopolysiloxane, a cross-linking agent and a catalyst, as at least one further constituent or as at least one component of further constituents, a substance that is still capable of flowing after the composition has been cross-linked, or a rod-shaped copolymer of styrene and n-butyl acrylate which is produced by copolymerising the said monomers by means of free radicals in the presence of diorganopolysiloxane, or containing both a copolymer of that type and a substance that is still capable of flowing after the composition has been cross-linked, and the cross-linking agent and the catalyst being combined in the composition only more or less shortly before the composition is applied to the base coating, characterised in that there is used as the base coating a layer that consists at least partly of a cross-linked organopolysiloxane having $\text{SiO}_{4/2}$ units, trimethylsiloxane units and vinyl dimethylsiloxane units, and a layer of an organopolysiloxane elastomer that is applied to the former layer and is at least partially cross-linked, which organopolysiloxane elastomer is produced from a composition that can be stored with the

exclusion of water and that cross-links on the admission of water at room temperature.

The process according to the invention is of especially great importance in the case of supports consisting of solid surfaces that are in water containing living organisms for such a long time that, if they were not treated, growth would form on them. Examples of surfaces of that type are surfaces made of glass, wood, plastics material, such as epoxy resin, including adhesive lacquers based on epoxide pitch, or glass-fibre-reinforced polyester, inorganic building material, such as concrete, or metal, for example iron or steel, and they are the surfaces of, for example, hulls of ships, buoys, sea-mines, the piers of drilling platforms or bridges, containers, including swimming pools, and pipes. The water containing living organisms to which the supports treated according to the invention may be exposed may be salt water or fresh water, especially salt water. The water may be stagnant or flowing.

Organopolysiloxane compositions that can be cross-linked at room temperature and into which a cross-linking agent and a catalyst are mixed more or less shortly before final use are so-called "two-component compositions" or "two-component systems".

The manufacture of two-component compositions that can be cross-linked to form organopolysiloxane elastomers and that contain, in addition to at least cross-linkable diorganopolysiloxane, a cross-linking agent and a catalyst, also a rod-shaped copolymer of styrene and n-butyl acrylate that is produced by copolymerising the said monomers, that is to say styrene and n-butyl acrylate, by means of free radicals in the presence of diorganopolysiloxane, has frequently been described and therefore need not be explained in detail again here. It is described in detail, for example, in Example 6 of US-PS 4 133 938, which was mentioned at the beginning, in

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Examples 6 and 8 of US 3 555 109 (issued 12th January 1971, I. C. Getson, Stauffer-Wacker Silicone Corporation), and in Example 6 of US 4 032 499 (issued 28th June 1977, F.-H. Kreuzer et al., Consortium für Elektrochemische Industrie GmbH). Compositions of that type are commercially available.

From 45 to 75% by weight of the rod-shaped copolymers produced by copolymerisation by means of free radicals in the presence of diorganopolysiloxane are preferably units derived from styrene, the remainder being units derived from n-butyl acrylate.

The amount of diorganopolysiloxane is preferably from 20 to 60% by weight, based on the total weight of the diorganopolysiloxane and the copolymer of styrene and n-butyl acrylate.

Owing, especially, to their ready accessibility, preferably at least 80% of the number of organic radicals in the diorganosiloxane units are methyl radicals.

The diorganopolysiloxanes in the presence of which the rod-shaped copolymer of styrene and n-butyl acrylate is produced preferably have an average viscosity of from 150 to 6,000 mPa.s at 25°C.

The substance that is still capable of flowing after the organopolysiloxane composition has been cross-linked to form an elastomer may be triorganosiloxy-terminated diorganopolysiloxane that is liquid at room temperature (see GB-PS 14 70 465, issued 14th April 1977, The International Paint Company Limited) or organic compounds that are capable of flowing and are free of metal and silicon (see DE-OS 2 756 495, published 22nd June 1978, Shell International Research Maatschappij B.V.) or, alternatively, mixtures of such flowable organic compounds and such flowable organopolysiloxanes. Also already known are two-component compositions that can be cross-linked to form organopolysiloxane elastomers and that contain both triorganosiloxy-terminated diorgano-

polysiloxanes that are liquid at room temperature, or other organic compounds that are still capable of flowing after the composition has been cross-linked, and also a rod-shaped copolymer of styrene and n-butyl acrylate produced by copolymerising the said monomers by means of free radicals in the presence of diorganopolysiloxane (see European Patent Application 0032597, (issued 29th July 1981, Shell Internationale Research Maatschappij B.V.)).

The most important examples of triorganosiloxy-terminated diorganopolysiloxanes that are liquid at room temperature are trimethylsiloxy-terminated dimethylpolysiloxanes, trimethylsiloxy-terminated methylphenylsiloxanes, trimethylsilane-terminated copolymers of dimethylsiloxane units and methylphenylsiloxane units, trimethylsiloxy-terminated copolymers of dimethylsiloxane units and diphenylsiloxane units, and trimethylsiloxy-terminated copolymers of dimethylsiloxane units, methylphenylsiloxane units and diphenylsiloxane units.

The most important examples of organic compounds that are capable of flowing and are free of metal and silicon are polyisobutylenes having a molecular weight of 350, technical white oil and tricresyl phosphate.

The substance that is still capable of flowing after the organopolysiloxane composition has been cross-linked to form an elastomer is present in that composition preferably in amounts of from 10 to 80% by weight, based on the total weight of the substance, the organopolysiloxane to be cross-linked and the rod-shaped copolymer of styrene and n-butyl acrylate that may be present.

The most important examples of cross-linking agents in two-component compositions of the type used within the scope of the invention are polyethyl silicate having an SiO_2 content of from 34 to 40% by weight, and hexaethoxydisiloxane.

The most important examples of catalysts in two-component compositions of the type used according to the invention are tin compounds, such as dibutyltin dilaurate and dibutyltin diacrylates, the acrylate groups being derived, in each case, from a mixture of carboxylic acids having from 9 to 11 carbon atoms per molecule, wherein the carboxy group, in the case of at least 90% by weight of the acids, is bonded to a tertiary carbon atom (so-called "dibutyltin diversatate").

The manufacture of layers, as base coatings, that consist at least partly of a cross-linked organopolysiloxane having $\text{SiO}_{4/2}$ units, trimethylsiloxane units and vinyltrimethylsiloxane units is known, and compositions for the manufacture of such layers are commercially available. In this respect, reference is made, for example, to the leaflet "Wackersilicone" SM 12-121. 803, April 1980, pages 1 and 2.

The manufacture of layers of an organopolysiloxane polymer produced from a composition that can be stored with the exclusion of water and that cross-links on the admission of water at room temperature is likewise known and has frequently been described. It therefore need not be discussed again here. Compositions of that type are also commercially available. Preferred compositions that can be stored with the exclusion of water and that cross-link on the admission of water at room temperature are those that free acetic acid or an amine, such as sec.-butylamine or cyclohexylamine, on cross-linking.

The base coatings used in the process according to the invention may be dissolved or dispersed in an organic solvent, such as toluene or a mixture of xylene isomers. Likewise, the two-component compositions used in the process according to the invention that can be cross-linked to form organopolysiloxane elastomers may be dissolved or dispersed in an organic solvent, such as white spirit.

The mixtures used within the scope of the process according to the invention can be applied to the supports, for example, by spreading, pouring, spraying or rolling.

In the following example and comparison test, all parts and percentages are by weight, unless otherwise stated.

Example

An adhesive lacquer based on epoxide pitch is applied to sheet steel. 72 hours after application, there is applied to that layer, by immersion, a mixture of

- 10 parts of polyethyl silicate having an SiO_2 content of approximately 34%,
- 10 parts of butyl titanate, and
- 10 parts of an organopolysiloxane having $\text{SiO}_{4/2}$ units, trimethylsiloxane units and vinyltrimethylsiloxane units in a molar ratio of 1 : 0.8 : 0.1, in the form of a 60% solution in toluene.

One hour after application of the mixture containing an organopolysiloxane, there is applied to the layer produced by that mixture, as the composition that can be stored with the exclusion of water and that cross-links to form an elastomer on the admission of water at room temperature, a composition produced by mixing

- 100 parts of a dimethylpolysiloxane having an Si-bonded hydroxy group in the terminal units and having a viscosity of approximately 80,000 mPa.s at 25°C,

with

- 20 parts of a silica having a specific surface area of 150 m^2/g , the silanol groups of which are partially replaced by trimethylsiloxy groups,
- 5 parts of methyltriacetoxysilane, and
- 0.5 part of di-tert.-butoxydiacetoxysilane.

Two hours after application of that composition, there is applied to the layer produced therefrom, using a spreading knife, a mixture of

100 parts of a mixture consisting, for its part, of
62.5 parts of a dimethylpolysiloxane having
an Si-bonded hydroxy group in each
terminal unit and having a viscosity of
approximately 1,000 mPa.s at 25°C,

62.5 parts of silica,

2 parts of ferric oxide, and

4 parts of calcium carbonate,

20 parts of a trimethylsiloxy-terminated dimethyl
polysiloxane having an average molecular weight
of approximately 16,000,

and, mixed in shortly before application,

3 parts of a mixture consisting, for its part, of

3 parts of polyethyl silicate having an
SiO₂ content of approximately 34%, and

1 part of dibutyltin acrylates, the acrylate
groups being derived, in each case, from a
mixture of carboxylic acids having from 9
to 11 carbon atoms per molecule, wherein
the carboxy group, in the case of at least
90% of the acids, is bonded to a tertiary
carbon atom,

as the composition that can be cross-linked to form an
elastomer and that contains, in addition to cross-
linkable diorganopolysiloxane, a cross-linking agent and
a catalyst, as at least one further constituent, a
substance that is still capable of flowing after the
composition has been cross-linked, the cross-linking
agent and the catalyst being mixed in only more or less
shortly before the composition is applied to the base
coating. Before noticeable cross-linking of the coating
begins, a thin strip of sheet steel, which has been
coated with the above-described adhesive lacquer

and then has also been coated in the manner indicated above, is placed on the coating in overlapping manner, likewise before noticeable cross-linking of the composition that can be cross-linked to form an elastomer begins, and is lightly pressed on.

The arrangement thus obtained is stored for 7 days at 23°C and a relative moisture content in the air ("air humidity") of 50%. The strip of sheet steel is then removed at a rate of 200 mm/minute. The shearing adhesive strength determined in that operation is 116 N/cm².

Comparison test

The procedure given in the Example is repeated, except that a mixture of

17 parts of butyl titanate,

11 parts of tetra-n-propylsilane,

8 parts of tetra(methoxyethylene)silane, and

4 parts of methyltris(methoxyethylene)silane

in the form of a 10% solution in white spirit is used as the base coating.

The shearing adhesive strength determined as given in the Example after 7 days' storage at 23°C and 50% air humidity is 92.4 N/cm².



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Patent Claims

1. Process for strengthening the adhesion of organopolysiloxane elastomers, produced from compositions that can be cross-linked at room temperature, to supports, by applying a base coating to the support before applying the composition that can be cross-linked to form the elastomer, this composition containing, in addition to cross-linkable diorganopolysiloxane, a cross-linking agent and a catalyst, as at least one further constituent or as at least one component of further constituents, a substance that is still capable of flowing after cross-linking has taken place, or a rod-shaped copolymer of styrene and n-butyl acrylate which is produced by copolymerising the said monomers by means of free radicals in the presence of diorganopolysiloxane, or containing both a copolymer of that type and a substance that is still capable of flowing after the composition has been cross-linked, and the cross-linking agent and the catalyst being mixed into the composition only more or less shortly before the composition is applied to the base coating, characterised in that there is used as the base coating a layer that consists at least partly of a cross-linked organopolysiloxane having $\text{SiO}_{4/2}$ units, trimethylsiloxane units and vinyltrimethylsiloxane units, and a layer of an organopolysiloxane elastomer that is applied to the former layer and is at least partially cross-linked, which organopolysiloxane elastomer is produced from a composition that can be stored with the exclusion of water and that cross-links on the admission of water at room temperature.

2. Process according to claim 1, characterised in that there is used as the composition that can be stored with the exclusion of water and that cross-links on the



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admission of water at room temperature, one that frees
acetic acid or an amine on cross-linking.