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# (54) A waterproof membrane.

(57) A waterproof membrane, such as may be used to create a flat roof, may be formed from a matrix which is impregnated with a curable composition. The matrix consists of a body formed from a plurality of fibres which may be woven or non-woven. This matrix is adapted to absorb the curable composition in a liquid state. The curable composition cures by polymerising to form a flexible waterproof material. The curable composition may comprise a silicone rubber material.

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# A WATERPROOF MEMBRANE

THE PRESENT INVENTION relate to a waterproof membrane and relates to a method of manufacturing a waterproof membrane.

There has, for a long time, been a requirement for a resilient and durable waterproof membrane which is economic and straight forward to manufacture.

It is envisaged that such a membrane may have many uses. For example, such a membrane may be utilised inconnection with flat roofs. At the present point in time a waterproof membrane is utilised, comprising "roofing felt", which consists of a fabric matrix coated with a bitumastic material. Such roofing felt only has a limited useful life, and the deterioration of the roofing felt is accelerated by exposure to ultra-violet light.

According to one aspect of this invention there is provided a waterproof membrane, said membrane comprising a matrix impregnated with a curable composition, the matrix consisting of a body formed from a plurality of fibres, the body being adapted to absorb the curable composition in a liquid state, the curable composition having cured to form a flexible waterproof polymer material.

Preferably the said curable composition comprises a composition which cures to form a silicone rubber material.

Conveniently said matrix consists of a non-biodegradable material.

Advantageously the matrix consists of a material made from polyester fibres.

Preferably the matrix is a non-woven matrix.

Conveniently the matrix has an initial thickness of 3 millimetres prior to impregnation.

Advantageously the curable composition comprises a mixture of a silicone polymer, a cross-linker, a plasticiser, an accelerator and a solvent.

Preferably the composition initially contains an inhibitor.

Conveniently the inhibitor comprises methyl ethyl ketoxine.

Advantageously the inhibitor is initially provided in a concentration of between 0.5 to 2 per cent by weight of the curable composition.

Preferably the inhibitor is provided in a concentration of 0.5 to 1 per cent by weight of the mixture.

Conveniently the curable composition is initially provided as the silicone polymer, the plasticiser and some solvent, and, separately, an accelerator and a cross-linking agent together with some solvent, the two components being mixed to form the curable composition before the matrix is impregnated with the curable composition.

Preferably the silicone polymer comprises a hydroxyl ended dimethyl polysiloxane.

Advantageously the silicone polymer has an initial viscosity of approximately 50,000 c.p.s.

Conveniently the cross-linker comprises a silane.

Preferably the cross-linker is an acetoxysilane.

Alternatively the cross-linker is a modified ketoximosilane.

Alternatively the cross-linker is a methyl ethyl ketoxine.

Conveniently the cross-linker is a mixture of methyl tris (methyl ethyl ketoxamino) silane with an amino silane.

Preferably the plasticiser is a silicone oil.

Alternatively the plasticiser is an alpha-w-dimethyl poly dimethyl siloxane.

Conveniently the plasticiser is in the form of a silicone oil having a viscosity of approximately 350 centistokes at 25°C.

Preferably the accelerator comprises an organo-tin compound.

Advantageously the accelerator is dibutyl-tin dilaurate.

Conveniently the solvent comprises 1,1,1,-trichloroethane.

Alternatively the solvent comprises a mixture of 1,1,1,-trichloroethane and white spirit.

Preferably the solvent comprises 50 per cent or more trichloroethane.

In some embodiments the solvent comprises 25 per cent or more trichloroethane.

Preferably the mixture consists of between 35 and 50 per cent by weight polymer, between 15 and 25 per cent by weight plasticiser, between 1 and 3 per cent by weight cross-linker and between 0.015 and 0.03 per cent accelerator, with solvent making the mixture up to 100 per cent.

Conveniently the mixture consists of 40-44 per cent by weight polymer.

Advantageously the mixture consists of between 18 to 22 per cent by weight plasticiser.

Preferably the mixture consists of between 2 to 2.5 per cent by weight cross-linker.

Conveniently the mixture comprises 0.02 to 0.025 per cent accelerator.

Preferably the viscosity of the mixture is initially within the range of 15 to 25 poise.

Advantageously the mixture has a viscosity within the range of 19 to 23.5 poise.

Conveniently the viscosity of the mixture is approximately 22 poise.

The invention also relates to a method of forming a waterproof membrane as described, the method comprising the steps of impregnating the matrix with the curable composition and permitting

the composition to cure.

Preferably the method comrpises the steps of coating a surface to be protected with the curable composition, applying the matrix to the coated surface and applying more curable composition to the exposed areas of the matrix so that the matrix is fully impregnated with the curable composition.

Conveniently the curable composition is initially sprayed on to the surface to be protected to form a coating of the curable composition and is finally sprayed on to the matrix when the matrix is in position.

In order that the invention may be more readily understood, and so that further features thereof may be appreciated, the invention will now be described, by way of example.

The invention provides a waterproof membrane which consists of a matrix which is impregnated with a curable silicone rubber material.

The matrix may be of any convenient form, provided it can absorb the silicone rubber material in the uncured state.

The matrix may consist of many alternate materials. The matrix may, for example consist of a biodegradable woven material, such as hessian, or may consist of a non-biodegradable material, that is to say a material made from a synthetic or man-made fibre such as polyester. It has been found that very good results are obtained using a non-woven material as the matrix, in the form of a fleece formed from a polyester fibres. The fleece is needled, but is not a woven fabric. Such a matrix presents a large number of randomly oriented fibres, defining a large number of interstices which can absorb the silicone rubber material in the uncured state. Of course, matrices of other particular forms may provide a similar effect. Thus a fabric woven from strands or filaments of polyester which present a large number of protruding fibres may well be found to be satisfactory, as may a material having a formation similar to that of velvet.

The preferred polyester fleece has a thickness, before impregnation, of approximately 3 millimetres.

In forming the waterproof membrane of the invention, the matrix is impregnated with a composition which cures or sets to form a silicone rubber. The composition with which the matrix is impregnated may consist of a mixture of a silicone polymer, a cross-linker, a plasticiser, an accelerator and a solvent. The composition may initially contain an inhibitor which will prevent the curing or setting reaction from taking place, the inhibitor being such that once the composition has been impregnated into the matrix the effect of the inhibitor terminates, thus enabling the curing or setting re-action to be completed. The inhibitor will, however, present the setting or curing re-action commencing while the composition is being stored prior to use.

It is envisaged that whilst the composition may be supplied in a single container or drum, with an inhibitor to prevent the setting or curing reaction, alternatively the material may be provided in two drums to be mixed on site, one drum containing the silicone polymer, the plasticiser and some solvent, and the other drum containing the accelerator and cross-linking agent together with some solvent. It is to be understood that in such a situation the contents of the two drums would be mixed immediately before the impregnating step.

The silicone polymer may be selected from a large number of readily available silicone polymers, and may, for example, be a hydroxyl ended dymethyl polysiloxane. It is preferred to utilise a silicone polymer having a viscosity of approximately 50,000 c.p.s., although polymers having a greater or lower viscosity may be utilised. The viscosity is, of course, a measure of the molecular weight of the polymer. The typical formula for the silicone polymer would be $HO-(Si(CH_3)_2-O)_n-H$

The cross-linking agent may be a silane. In some cases it may be appropriate to use an acetoxysilane of the type having the formula $(R)_4-N-Si-(O.CO.CH_3)_n$ where R is one of the radicals $-CH_3$; $-CH_2.CH_3$; or $-O-C-(CH_3)_3$. One disadvantage of such cross-linking agents is that during the curing or setting stage acetic acid fumes are generated, which in certain circumstances can be very disadvantageous, especially if the setting or curing reaction is being carried out within a confined space. Thus it is preferred to use as a cross-linking agent a modified ketoximosilane or a methylethylketoxine. The preferred cross-linking agent is a mixture of methyl tris (methyl ethyl ketoxamino) silane with an amino silane. Such a mixture is sold by ICI under the trade designation Silcane Sealant Cross-linking Agent Number 8.

The plasticiser utilised may be a silicone oil such as an alpha-w-dimethyl poly dimethyl siloxane, as sold by ICI under the trade designation F 111. The oil preferably has a viscosity of 350 centistokes at 25°C, although much higher viscosities may prove to be satisfactory in practice.

The accelerator utilised may be an organo-tin compound and is preferably dibutyl tin dilaurate, but other materials may be utilised such as stannous octoate or a platinum salt.

Whilst any appropriate solvent may be utilised it is preferred to use 1,1,1,-trichloroethane, or a mixture of 1,1,1,-trichloroethane and white spirit. In such a mixture prferably there is 50 per cent or more trichloroethane. If the trichloroethane concentration is reduced to 25 per cent the resultant mix is, at ordinary temperatures, very viscous.

The preferred mixture of these components, consists of between 35 and 50 per cent by weight

polymer, preferably 40 to 44 per cent weight polymer, between 15 and 25 per cent by weight plasticiser, preferably 18 to 22 per cent by weight plasticiser, between 1 and 3 per cent by weight cross-linker, preferably 2 to 2.5 per cent by weight cross-linker, and between 0.015 and 0.03 per cent accelerator, preferably 0.02 to 0.025 per cent accelerator. Solvent is used to bring the mixture up to 100 per cent. The preferred viscosity of the mixture is within the range of 15 to 25 poise, preferably being within the range of 19 to 23.5 poise, the most preferred viscosity being 22 poise.

During the curing process the silicone polymer molecules cross-link, thus forming a rubber having a very high molecular weight.

It may be found that less accelerator is necessary in hot weather.

If an inhibitor is provided it may be methyl ethyl ketoxine and may be provided to comprise 0.5 to 2 per cent by weight of the mixture, preferably 0.5 to 1 per cent by weight.

The matrix may be impregnated with the composition that cures to form silicone rubber by passing the matrix, utilising a series of rollers, through a bath containing the mixture described above. The matrix will be caused to pass through the bath for such a period of time that the matrix is fully impregnated with the mixture, and the matrix is then withdrawn from the bath. As the matrix leaves the bath, so the curing or setting reaction will commence, and the material absorbed by the matrix will set to form a silicone rubber material. The silicone rubber material is flexible but has significant strength, the strength being enhanced by the matrix which is fully embedded therein. The silicone rubber is resistant to ultra-violet light and maintains flexibility over a very wide range of temperatures between at least -60°C and +150°C. The membrane thus created is waterproof, but is gas permeable.

It is envisaged that when the silicone rubber has cured the membrane may be rolled into rolls for storage and transportation. The membrane may find many uses and may thus be used as a roofing material, or a material to line tanks, or may be used as a packaging material.

It is envisaged that particular benefits may arise if the matrix is impregnated with the mixture that sets to form the silicone rubber in situ . Thus, if a flat roof is to be provided with a waterproof membrane it is envisaged that after the roof has been prepared, the roof would be sprayed or otherwise coated with a preliminary layer of the mixture which sets to form the silicone rubber as described above. This mixture will therefore enter all the nooks and crannies present on the roof. Subsequently the matrix, in form of the polyester fleece described above will be located in position on top of the initial layer of curable material. The fleece will be cut to size so that, as far as is practicable, the entire surface of the initial layer of the curing composition is covered with at least one layer of the fleece. At the edges of the discrete elements of fleece, the fleece may overlap itself. Subsequently a further layer of the curable material is applied to the top surface of the fleece, this layer fully impregnating the fleece. The curable composition is then left to cure. The end result is that since the fleece is fully impregnated, all the curable composition sets to form effectively an integral layer or element of silicone rubber in which the fleece is fully embedded. The layer of silicone rubber is firmly adhered to the roof sub-structure, thus providing a durable waterproof coating. Since the silicone rubber material is inherently flexible, even if the sub-structure of the roof should move, due to settlement, or due to thermal expansion and contraction, the silicone rubber will be able to accommodate such movement without tearing and without otherwise being damaged. Even if the roof is exposed to direct sunlight, which contains ultra-violet light, the silicone rubber material will not deteriorate. It is envisaged that a roof, provided with a waterproof membrane in the manner described above, may prove to be weather-tight for a period of at least 50 years.

It is envisaged that waterproof membranes as described above may find many different applications. It will readily be appreciated that such a waterproof membrane may be utilised as a tank lining, or as a lining for a swimming pool, or as a lining for a basement or other parts of a building subjected to damp. Such a membrane may be incorporated within the foundations of a building, particularly if the building is of the type which is formed with an integral concrete floor slab. However, it is also envisaged that a waterproof membrane as described may find other applications. For example, such a waterproof membrane may be provided on the exterior of items of machinery which operate within a hostile environment, such as pumps as used in waterworks, sewage farms or the like. At the present point in time any such pumps have to be fabricated from corrosion-resistant material, such as stainless steel, which means that such pumps are very expensive. However, it is envisaged that the exterior of such a pump may be provided with a protective coating effectively formed from a waterproof membrane as described above, thus enabling the pump to be manufactured initially of a much cheaper material.

It is envisaged that the curable mixture may, if desired, contain appropriate dyes or colourants, so that the membrane, when manufactured, has a desired colour.

The invention will be described with reference

to the following specific examples.

## EXAMPLE 1

A fleece was formed of needled felt using 100 per cent 1.5 decitex fibres of polyester. The felt was unspported, in that it did not have a scrim in the middle of it. The felt had an initial weight of 220 g/M$^2$ and it was heat set for stabilization.

## EXAMPLE 2

A curable composition was fabricated by mixing together 42 per cent by weight of a silicone polymer consisting of a hydroxyl ended dimethyle polysiloxane having a viscosity of 50,000 c.p.s., 20 per cent by weight of a plasticiser consisting of an alpha-w-dimethyl poly dimethyl siloxane (as sold by ICI under the trade designation F 111), 2.25 per cent by weight of a cross-linking agent consisting of a mixture of methyl tris (methyl ethyl ketoxamino) silane with an amino silane (as sold by ICI under the trade designation Silicone Sealant Cross-linking Agent Number 8) 0.225 per cent by weight of an accelerator consisting of dibutyle-tin dilaurate, 1 per cent of an inhibitor consisting of methyl ethyl ketoxine and, to 100 per cent, a solvent consisting of 1,1,1,-trichloroethane mixed with an equal quantity of white spirit.

## EXAMPLE 3

During the construction of a tunnel, after the metallic tunnel lining had been located in pos ition, the interior of the tunnel lining was sprayed with the curable composition as fabricated in Example 2. Immediately after the spraying, fleece, as described in Example 1, was applied to the interior of the tunnel, the fleece being bonded to the interior of the tunnel with the sprayed on composition, which was beginning to cure. Part of the composition was, however, absorbed into the fleece. Subsequently more of the curable composition of Example 2 was sprayed on to the exterior of the fleece, again being absorbed into the fleece until the fleece was totally impregnated. The inhibitor evaporated from the curable composition, permitting a cross-linking reaction to proceed, until the curable composition was fully cured. The tunnel was found to have an interior lining comprising a waterproof membrane. The membrane was slightly flexible and resilient, and was thus able to withstand thermal expansion and contraction of the tunnel lining. The material was not rigid and was able to withstand vibrations within the tunnel.

## EXAMPLE 4

The roofing felt covering a flat roof had perished. The roofing felt was removed, revealing the roof sub-structure. Necessary repairs were effected to the roof sub-structure where it had been exposed to damp penetrating through the roofing felt. A coating of the curable composition of Example 2 was applied to the roof sub-structure so as to fully cover the roof sub-structure and pene trate all the nooks and crannies of the roof. The composition was also sprayed on to the lower part of an upstanding wall partly bounding the roof. Subsequently a fleece as described in Example 1 was applied to the entire roof area, with separate elements of the fleece overlapping each other at their adjacent edges. The initial sprayed-on composition was partly absorbed into the fleece. Subsequently a second layer of the curable composition was sprayed on to the exposed surface of the fleece, this second layer being fully absorbed by the fleece so that the fleece was fully impregnated with the curable composition of Example 2. The composition of Example 2 was left to cure, by permitting the inhibitor to evaporate, thus enabling the cross-linking reaction to complete.

The roof was found to be coated with a very tough but yet resilient waterproof membrane. High pressure water jets were directed at the roof to test the quality of the waterproof membrane, and no moisture was found to penetrate the membrane.

## Claims

1. A waterproof membrane, said membrane comprising a matrix impregnated with a curable composition, the matrix consisting of a body formed from a plurality of fibres, the body being adapted to absorb the curable composition in a liquid state, the curable composition having cured to form a flexible waterproof polymer material.

2. A waterproof membrane according to Claim 1 wherein the said curable composition comprises a composition which cures to form a silicone rubber material.

3. A waterproof membrane according to Claim 1 or 2 wherein said matrix consists of a non-biodegradable material.

4. A waterproof membrane according to Claim 3 wherein the matrix consists of a material made from polyester fibres.

5. A waterproof membrane according to any one of the preceding Claims wherein the matrix is a non-woven matrix.

6. A waterproof membrane according to any one of the preceding Claims wherein the matrix has an initial thickness of 3 millimetres prior to impregna-

tion.

7. A waterproof membrane according to any one of the preceding Claims wherein the curable composition comprises a mixture of a silicone polymer, a cross-linker, a plasticiser, an accelerator and a solvent.

8. A waterproof membrane according to Claim 7 wherein the curable composition is initially provided as the silicone polymer, the plasticiser and some solvent, and, separately, an accelerator and a cross-linking agent together with some solvent, the two components being mixed to form the curable composition before the matrix is impregnated with the curable composition.

9. A waterproof membrane according to Claims 7 or 8 wherein the mixture consists of between 35 and 50 per cent by weight polymer, between 15 and 25 per cent by weight plasticiser, between 1 and 3 per cent by weight cross-linker and between 0.015 and 0.03 per cent accelerator, with solvent making the mixture up to 100 per cent.

10. A method of forming a waterproof membrane according to any one of the preceding claims wherein the method comrpises the steps of coating a surface to be protected with the curable composition, applying the matrix to the coated surface and applying more curable composition to the exposed areas of the matrix so that the matrix is fully impregnated with the curable composition.

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number

EP 90 31 0413

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.5) |
|---|---|---|---|
| X | EP-A-0 073 564 (DOW CORNING CORP.)<br>* claims 1-5 * * example 2 * | 1-10 | D 06 N 5/00<br>D 06 N 3/12 |
| X | EP-A-0 071 339 (DOW CORNING CORP.)<br>* page 26, line 3 - page 27, line 3; claims 1-3 * | 1-5,7,10 | |
| A | DE-A-2 621 333 (K. ZEISS)<br>* claims 1-3; figure 1 * | 1 | |

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

D 06 N
C 08 J

The present search report has been drawn up for all claims

| Place of search | Date of completion of search | Examiner |
|---|---|---|
| The Hague | 14 December 90 | PFANNENSTEIN H.F. |

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
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P: intermediate document
T: theory or principle underlying the invention

E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document