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(54) Roofing membrane comprising microspheres

(57) A foam suitable for use in roofing systems is provided. Roofing membranes comprising the foam have superior flowing properties at high temperatures without sacrificing low temperature performance. A particular useful roofing membrane comprises an upper surface layer, a reinforcement layer, and optionally a lower self-adhesive layer, wherein expanded microspheres are provided in one or more of said layers in an amount of between 0.01 and 10% based on the total weight of the roofing membrane. Moreover a method of making roofing membranes is provided.

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Description

[0001] The present invention relates to a foam in roofing systems for achieving superior flowing properties at high temperatures without sacrificing low temperature performance. More particularly, the present invention is in the field of roofing membranes and shingles, having a modified bituminous compound on the top surface, wherein microspheres are employed in the bituminous compound in order to achieve superior flowing properties.

Roofing membranes

[0002] Of the two general types of bituminous sheet materials used for roofing applications, i.e., bitumen-SBS and bitumen-APP materials, the bitumen-SBS products are more elastic, with greater flexibility at low temperatures.

[0003] The waterproofing properties of a bituminous membrane depend upon the existence of continuous films of bitumen. To prevent rupture or flow of the bitumen a sheet material (felt) is normally incorporated. Felts add strength and spanning ability to the membrane but may, in turn, be responsible for membrane failures. A bituminous membrane acts as a single composite structure, but its behaviour is influenced by the properties of the materials from which it is made, the surface to which it adheres, and the environment in which it must serve.

[0004] Bitumen, a material that behaves as a viscous fluid at some temperatures and as an elastic solid at lower ones, has been employed for centuries in construction because of its waterproofing and adhesive properties. Through long experience many of its limitations have been recognized, but improved understanding of the factors affecting its performance has been gained through scientific research.

[0005] The waterproofing capability of bitumen is primarily a result of its nonporous characteristic. Although absorption of water by bitumens does occur, it is generally very limited and of little significance. For bitumen to perform as a water barrier there must be a continuous film free of any voids, pin holes or cracks. Provided this continuity is achieved the film can be as little as 0.005 inch thick, but deterioration of bitumen and other practical considerations usually dictate the use of a much thicker film.

[0006] The cohesion, or internal strength, and the flow properties of bitumens vary considerably with temperature and stress conditions. Bitumen behaves in a viscoelastic manner, and under the influence of an applied strain its deformation will depend upon the rate of strain and the temperature at which it occurs. At a warm temperature bitumen behaves as a liquid; at lower temperatures it behaves as an elastic solid. As the behaviour of both solid and liquid materials is involved, any mechanical properties such as load-strain must be related to the rate of deformation and temperature.

[0007] Deterioration, or loss of the desirable properties of bitumen, normally takes the form of hardening. The net result is a decrease in adhesive and flow properties and an increase in the softening point temperature and coefficient of thermal expansion. Hardening of a bitumen results in a reduction in its ability to accommodate deformations without splitting. The actual mechanisms of deterioration are not fully understood, but it is known that photo-oxidation is a major factor and that it is most active at high temperatures under solar radiation. Water, dissolved compounds from atmospheric pollution, attack by microbiological organisms, and changes in its internal structure are other factors contributing to hardening of bitumens.

[0008] Reinforcement is employed in a bituminous membrane to stabilize the bitumen film, to provide the strength required to span irregularities in its supporting surface, and to distribute local strains over a greater dimension. Adhesion between the bitumen films and reinforcement is essential, and it is normal to factory prime these materials by saturating them with hot bitumen. Bitumen saturation also minimizes the water absorption of felts, but since saturation is not complete they do absorb moisture and are not vapor impermeable. Bitumen coating of saturated felts further reduces the vapor permeance and increases the resistance to moisture penetration.

[0009] The manufacture of bituminous roofing material with multiple layers is well-known. For example, U.S. Pat. Nos. 2,893,889; 4,755,409; 4,871,605; and EP Patent No. 903435 disclose membranes comprised of a core and a plurality of different layers of waterproofing material. The ’409 patent also discloses a release sheet applied to the one side of the membrane for purposes of protection. Products are in the market, which combine the more flexible and elastic bitumen-SBS upper layer with a self-adhesive lower surface.

[0010] Bituminous roofing materials are used in e.g. steep slope roofing applications and, therefore, must provide good traction for the safety of the roofer installing the material. A typical installation involves mechanically fastening the material to a substrate. Alternatively torching may be applied to the roofing material. Less commonly the roofing material is adhered to the substrate using an adhesive compound.

[0011] It is essential to note that in hot areas the material must withstand high temperature without being deformed. This sometimes poses severe problems with roofing products that are modified with a styrene-butadiene-styrene (SBS) compound, which softens and flows at temperatures above 110 degrees Celsius. Hence it is necessary to develop a product that has high heat resistance with minimal impact on the flexibility of the cold material.

[0012] Roofing membranes typically comprise multiple layers of various materials configured to protect and optionally to insulate a roof deck or upper surface of a structure or building. The roofing system protects the deck and the interior of the structure from the weather, including wind, rain, and other precipitation.

[0013] The roofing membrane is a sheet or mat of a solid, elastomeric substance, which protects the deck from the aforementioned weather elements. Conventional membranes include those of EPDM (ethylene-propylenediene elastomer), modified bitumen, and plasticized polyvinylchloride.

[0014] Optionally, a paving layer may be placed or laid on top of the membrane. The paving layer typically comprises materials such as gravel or stone ballast, shingles, brick, or concrete. The paving layer functions to physically protect the membrane from foot traffic and direct exposure to sunlight and the weather.

[0015] A problem commonly encountered with roofing systems is rupture of the membrane due to distortion or deterioration of the protective layer underneath the membrane. The distortion and deterioration problems arise from the exposure of the protective layer to extreme heat from direct sunlight or moisture buildup due to weather exposure. The membrane, which is typically dark and elastomeric, absorbs significant heat from the sunlight, and further does not allow for timely escape of moisture trapped underneath it. When the insulating and/or protective layer becomes distorted or deteriorated, the membrane and the protective layer may separate to form void pockets, which leave the membrane with diminished mechanical support on its undersurface. The diminished support renders the membrane more subject to rupture.

[0016] The source of distortion and deterioration problems of the material in the protective layer varies according to the nature of the material. Some materials are susceptible to heat, some are susceptible to moisture, and some have inherently low mechanical strength.

Microspheres and foams

[0017] Extruded, closed-cell polystyrene foams offer excellent mechanical strength and water resistance, but can become distorted at high service temperatures due to their relatively low heat distortion temperature. Such high service temperatures are typically encountered under a dark membrane in direct sunlight.

[0018] Expanded polystyrene bead foams typically better maintain their shape in a high temperature environment than extruded, closed-cell polystyrene foams because they typically have better bowing characteristics. Their bowing characteristics are better because the coalesced expanded bead structure allows for greater mechanical relaxation compared to the solid, cellular form of extruded, closed-cell foams. However, the coalesced expanded bead structure also results in lower mechanical strength and lower resistance to water transmission.

[0019] Closed-cell polyisocyanate foams have high heat distortion temperatures but have poor moisture resistance. Moisture weakens the cellular structure of such foams, and renders them subject to physical deterioration over time. Moisture also diminishes the insulation value of the foam. They are also relatively friable, which affects their handling characteristics. Closed-cell polyurethane foams, like closed-cell polyisocyanate foams, have high heat distortion temperatures and poor moisture resistance. They are also relatively friable, which affects their handling characteristics.

[0020] Expandable thermoplastic polymer beads are microspheres each comprising a thermoplastic polymer shell and a blowing agent as entrapped therein. When such expandable beads are heated at a temperature high enough to induce a sufficient degree of expansion for a certain length of time, expanded thermoplastic polymer beads are obtained. For example, when expandable micro sphere beads measuring about 15 μm in diameter and having a true specific weight of about 1.3 Kg/l are expanded by heating, expanded micro spheres measuring about 60 μm and having a true specific weight of about 0.03 kg/l may be obtained

The expanded micro sphere can be obtained by heating the expandable micro sphere at a predetermined temperature. The expanded micro sphere is a balloon-like artefact which can be imaged as a small rubber ball. The expandable micro sphere is a thermally expandable micro sphere comprising a thermoplastic polymer shell and a blowing agent as entrapped therein.

[0021] The thermoplastic polymer which can be used in the present invention includes polymers obtainable by polymerizing various monomers such as (meth)acrylonitrile, (meth)acrylates, styrenic monomers, vinyl halides, vinylidene halides, vinyl acetate, butadiene, vinylpyridine, chloroprene, etc; all of which may contain other comonomeric substances and crosslinking agents, such as divinylbenzene, ethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, 1,3-butylene glycol di(meth)acrylate, allyl (meth)acrylate, triacrylformal, triallyl isocyanurate, etc. Among them, the homopolymers, copolymers or terpolymer of at least one monomer selected from among methyl methacrylate, acrylonitrile and vinylidene chloride are especially useful.

[0022] The blowing agent (foaming agent) for causing thermal expansion of the micro spheres have a boiling point not higher than the softening temperature of the thermoplastic polymer shell and includes n-pentane, isopentane, neopentane, butane, isobutane, hexane, isohexane, neohexane, heptane, isoheptane, octane and isooctane, or mixtures thereof, to mention just a few preferred examples. Aside from them, hydrocarbons such as petroleum ether, etc. and chlorinated hydrocarbons such as methyl chloride, methylene chloride, dichloroethane, dichloroethylene, trichloroethane, trichloroethylene, etc. can also be used.

[0023] The weight average particle diameter of expandable micro spheres is preferably about 1-100 μm. The true specific weight of the expandable micro spheres is preferably about 1.1-1.5 kg/l. Heating the expandable micro sphere at a predetermined temperature gives the expanded micro sphere. The heating can be effected by various methods such as air heating, steam heating, microwave heating, infrared or far-infrared heating, etc.

[0024] The expandable micro spheres mentioned above are commercially available and any of such commercial products can be utilized.

[0025] The art of making cellular thermoplastic products is very well developed. It has long been known, for example in extrusion and molding processes, to form expanded thermoplastic products having a cellular structure by the injection of a gas under pressure into molten thermoplastic materials. Of the more recent patent literature, U.S. Pat. Nos. 2,98,130; 3,268,636; 3,436,446 and 3,975,473 are examples of such processes. These patents, however, are merely illustrative and it is not intended to suggest that they are the only or most pertinent background patents. Such patents disclose the widely used technique of injecting gas under high pressures into an extruder or barrel for solubilization in a thermoplastic melt, followed by discharge of the melt under reduced pressure thereby resulting in the production of foam.

[0026] Techniques are disclosed for making hot melt thermoplastic adhesive foams in U.S. application Ser. No. 710,377, filed Aug. 2, 1976 entitled "Hot Melt Thermoplastic Adhesive Foam System" now U.S. Pat. No. 4,059,714 and U.S. application Ser. No. 710,378, filed Aug. 2, 1976 for "Hot Melt Thermoplastic Adhesive Foam System" now U.S. Pat. No. 4,059,466. These applications are directed to methods of making and using hot melt foamed adhesives which offer significant improvements over conventional non-foamed adhesives. According to the techniques described in these applications, the gas is intimately mixed with a thermoplastic adhesive while the adhesive is in a molten state and then the mixture is pressurized to form a solution which, upon dispensing at a lower pressure, releases the gas and foamed adhesive results. The techniques described in these applications result in very useful foamed adhesives and bonding techniques. However, such techniques are not entirely satisfactory in producing hot melt thermoplastic adhesives on a continuous, uniform quality basis. Such techniques have also been found to be limited in their applicability to hot melt thermoplastic materials and further improvements are needed.

Objects of the invention

[0027] Many of the undesirable characteristics of bitumens can be modified by the addition of specially formulated compounds. There are a number of additives that improve adhesion properties, making it possible for bitumens to adhere to a wet surface and even retain their bond when later wetting of the bitumen-solid interface occurs. Anti-oxidants retard the rate of hardening from chemical and internal structure changes resulting from oxidation. However the problems with flowing bituminous roofing materials at higher temperatures still remains to be solved.

[0028] The common art roofing membranes function within a temperature range; if it is exceeded the product will melt and flow or freeze and become brittle. It is well known in the art to shift the interval to lower temperatures or to higher. But it has shown to be very difficult to change the width of this interval.

[0029] Hence it would be desirable to provide bituminous roofing materials which resist softening and flow at high temperatures, while maintaining plasticity at low temperatures. Thereby it would be possible to use the roofing material on sloped or even vertical substrates under hot climate conditions without sacrificing the cold properties.

[0030] The major object of the present invention is to provide a high temperature resistant roofing membrane without sacrificing the low temperature performance of the membrane.

Surprisingly by foaming the roofing membrane with microspheres it is possible to improve the flow resistance at high temperatures with minimal effect on the flow resistance at low temperatures. The density of the microsphere foamed membranes of the present invention is approx. 25% lower than membranes not employing a foam.

[0031] The present invention involves roof coverings in the form of roofing membranes and shingles having an upper layer of a modified bituminous compound, whose composition utilizes bitumen, plastomeric modifiers and fillers, a reinforcement layer, and optionally a lower layer of a self-adhesive compound, whose composition utilizes bitumen (asphalt), elastomeric modifiers, tackifying resins, and fillers. The expanded microspheres may be distributed across the entire membrane, but is preferably only used in the top layer.

[0032] According to the present invention there is provided a roofing membrane comprising:

an upper surface layer,
a reinforcement layer, and
optionally a lower self-adhesive layer,

wherein expanded microspheres are provided in one or more of said layers in an amount of between 0.01 and 10% based on the total weight of the roofing membrane.

Example

[0033] The top-layers of membranes having no microspheres and membranes including commercially available expanded microspheres (Expancel 095) were made using the following blends:

	1	2
Nynäs B250	61.6	61.0
Kraton 1184	8.4	8.3
Nordkalk kö100	30	29.7
Expancel 095		1.0
TOTAL	100	100

[0034] The blends are made on the diaf mixer at a mixing temperature of 180 °C, according to normal procedure.

[0035] Expancel is added after the filler. The addition is timed in such a way that the Expancel is mixed for 15 minutes after the addition.

[0036] The following table summarises the results:

	1	2
Melting point R&B (°C)	126.4	133.2
Cold bend pass (°C)	-24	-20
Density (kg/l)	1.34	1.07
Viscosity Brookfield (mPas)		
160°C	11094	36583
180°C	4317	13000
200°C	2100	3583
Flow, time to flow > 50mm, at 280 °C	48h	>>2 weeks
Resistance to footprints (Deformation: load: 2499 g/cm^2; time: 1 min; temperature: 60 °C)		
Reduction of thickness:		
When load is removed:	84%	82%
After 15 min at 60 °C	0%	*
After 2 hours at 60 °C	0%	*
After 3 hours at 60 °C	0%	0%

[0037] The cold bend temperature of the foamed blend is 4 °C higher than for the non-foamed blend, while the melting point R&B of the foamed blend is 6.8 °C higher. The flow resistance is measured using only the weight of the membrane itself. The time to 50mm flow is 48 hours for the non-foamed blend, while it is well in excess of two weeks for the foamed blend.

[0038] From the above it is seen that by foaming it is possible to improve the flow resistance of a blend with only a minimal impact on the cold bend.

[0039] The density of the non-foamed blend is approx. 25% higher than for the foamed blend.

[0040] The handling of foamed and non-foamed membranes was compared using the 0.4m times 1.0m test specimens. With these specimens we do not find any difference in the stiffness/flexibility of the membranes. A manual test of the adhesion of the slate does not suggest any difference in adhesion of slates on foamed and non-foamed bitumen.

[0041] The resistance against footprints is at the same level for the foamed and the non-foamed product.

[0042] The size distribution of the air bubbles was found by taking microscope pictures and then counting the bubbles and measuring their sizes. Expancel has provided a size distribution curve for Expancel 095D120 expanded in air for comparison.

[0043] It is seen that the size distribution of an unaged foamed sample is in the same interval as the curve given by Expancel. However the size distribution of the unaged foamed sample is much wider than the curve from Expancel. This indicates that there is still a possibility to improve the yield of the Expancel in bitumen.

[0044] The size distribution for a foamed sample that was kept at 180 °C for 24 hours is very close to the curve for the unaged sample; this indicates that the blend can be kept at elevated temperatures for some time without loosing the bubbles. A second foamed sample was kept at 190 °C for one hour; it can be seen that the size distribution moves towards higher sizes. So it would seem that there is an upper limit for the temperature the blends can be kept at for a longer period, without changing the characteristics.

Claims

1. a roofing membrane comprising:

- an upper surface layer
- a reinforcement layer, and
- optionally a lower self-adhesive layer,

wherein expanded microspheres are provided in one or more of said layers in an amount of between 0.01 and 10% based on the total weight of the roofing membrane.

2. The membrane of claim 1, wherein the lower self-adhesive layer is discretely distributed, preferably in form of stribes or patches, over the reinforcement layer.

3. The membrane of claims 1 or 2 further, wherein at least the upper surface layer comprises modified bitumen.

4. The membrane of any one of claims 1 to 3, wherein the expanded microspheres are based on polymers obtainable by polymerizing monomers selected from the group consisting of (meth)acrylonitrile, (meth)acrylates, styrenic monomers, vinyl halides, vinylidene halides, vinyl acetate, butadiene, vinylpyridine, and chloroprene.

5. The membrane of claim 4, wherein further comonomeric substances and crosslinking agents are selected from the group consisting of divinylbenzene, ethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, 1,3-butylene glycol di(meth)acrylate, allyl (meth)acrylate, triacrylformal, and triallyl isocyanurate.

6. A method of making the roof membrane of claim 1 comprising:

- providing a reinforcement layer having top and bottom surfaces,
- coating a microsphere-containing modified bitumen in a molten state on the top surface of said reinforcement layer,
- coating an adhesive layer on the lower surface of said reinforcement layer, and
- solidifying the molten embossed layers by cooling the membrane to room temperature.

8. Microsphere-containing bitumen for use in manufacturing a roofing membrane according to any one of claims 1 to 5.

9. Use of microspheres in the preparation of bitumen for extending the temperature interval in which the bitumen remains flow resistant.

10. Method for preparing a microsphere-containing bitumen comprising the steps of heating and melting a bitumen product, adding expanded microspheres and cooling the bitumen so as to obtain a foamed bitumen product.

11. Method for preparing a microsphere-containing bitumen comprising the steps of adding expandable microspheres to a bitumen product, heating until at least a part of the expandable microspheres expand, and cooling the bitumen so as to obtain a foamed bitumen product.

Amended claims in accordance with Rule 86(2) EPC.

1. a roofing membrane comprising:

- an upper surface layer
- a reinforcement layer, and
- optionally a lower self-adhesive layer,

wherein pre-expanded microspheres are provided in one or more of said layers in an amount of between 0.01 and 10% based on the total weight of the roofing membrane, said microspheres having been expanded before being added to the roofing membrane.

2. The membrane of claim 1, wherein the lower self-adhesive layer is discretely distributed, preferably in form of stribes or patches, over the reinforcement layer.

3. The membrane of claims 1 or 2 further, wherein at least the upper surface layer comprises modified bitumen.

4. The membrane of any one of claims 1 to 3, wherein the expanded microspheres are based on polymers obtainable by polymerizing monomers selected from the group consisting of (meth)acrylonitrile, (meth)acrylates, styrenic monomers, vinyl halides, vinylidene halides, vinyl acetate, butadiene, vinylpyridine, and chloroprene.

5. The membrane of claim 4, wherein further comonomeric substances and crosslinking agents are selected from the group consisting of divinylbenzene, ethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, 1,3-butylene glycol di(meth)acrylate, allyl (meth)acrylate, triacrylformal, and triallyl isocyanurate.

6. A method of making the roof membrane of claim 1 comprising:

- providing a reinforcement layer having top and bottom surfaces,
- coating a microsphere-containing modified bitumen in a molten state on the top surface of said reinforcement layer,
- coating an adhesive layer on the lower surface of said reinforcement layer, and
- solidifying the molten embossed layers by cooling the membrane to room temperature.

7. Microsphere-containing bitumen for use in manufacturing a roofing membrane according to any one of claims 1 to 5.

8. Use of microspheres in the preparation of bitumen for extending the temperature interval in which the bitumen remains flow resistant.

9. Method for preparing a microsphere-containing bitumen comprising the steps of heating and melting a bitumen product, adding expanded microspheres and cooling the bitumen so as to obtain a foamed bitumen product.

10. Method for preparing a microsphere-containing bitumen comprising the steps of adding expandable microspheres to a bitumen product, heating until at least a part of the expandable microspheres expand, and cooling the bitumen so as to obtain a foamed bitumen

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 04 07 8109

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	8 September 2005	Vratsanou, V

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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