(57) Abrégé/Abstract:
The invention relates to vacuum insulation panels (VIP) that consist of a microporous sheet as core layer and a plastic film coating that comprises at least 7 layers of the following sequence of layers: (1) polyolefin hot-seal layer (I), (2) adhesive or linking layer (II), (3) gas barrier layer (III), (4) adhesive or linking layer (II), (5) polyolefin layer (IV), (6) adhesive or linking layer (II), (7) a layer (V) that consists substantially of polyester and/or polyamide and/or polypropylene and that is vaporized with aluminum or SiOx or a metal oxide of the 2nd or 3rd main group.
Vacuum Insulation Panels

Abstract

Vacuum insulation panels (VIPS) having a microporous sheet as core layer and a covering of a plastics film comprising at least 7 layers in the layer sequence

(1) polyolefin heat-sealable layer (I)
(2) adhesive or bonding layer (II)
(3) gas barrier layer (III)
(4) adhesive or bonding layer (II)
(5) polyolefin layer (IV)
(6) adhesive or bonding layer (II)
(7) a layer (V) consisting substantially of polyester and/or polyamide and/or polypropylene sputtered with aluminium or SiOx or a metal oxide of the 2nd or 3rd main groups.
**Vacuum Insulation Panels**

The present invention relates to vacuum insulation panels having an improved insulating effect, a gas diffusion-impermeable plastics film suitable for the production of such vacuum insulation panels, and the use of such vacuum insulation panels in refrigeration equipment.

Vacuum insulation panels ("VIP"), being excellent insulating materials, have attracted a great deal of interest in all areas of thermal insulation, but especially in domestic refrigeration equipment. As a rule they are superior to rigid polyurethane foams, which are normally used in domestic refrigeration equipment, by a factor of more than two as regards their insulating effect. Normally vacuum panels are produced by a process in which microporous supporting materials are covered with films and welded *in vacuo*. The pressure in a VIP is normally less than 1 mbar, for only at such low pressures is the requisite insulating effect achieved. Among present-day VIPs, in principle two types should be distinguished:

microporous precipitated silicic acid covered with plastics film corresponding to EP 0 463 311 or DE 40 19 870 A1, EP 0 396 961 B1 and EP 0 446 A2 or DE 40 08 480, and microcellular plastics foams covered with an aluminium composite film, such as are described for example in US Patent 4,669,632.

The disadvantage of VIPs based on a core layer of microporous precipitated silicic acid is that a pulverulent material is used as starting material and accordingly the VIPs have significant thickness tolerances and deviations from planarity that complicate the incorporation in refrigeration equipment.

The disadvantage of VIPs based on a core layer of plastics foams is that plastics foams have only a very small absorption capacity for gases, in particular water vapour, with the result that the gas-tightness of the film used for the application of these otherwise outstandingly suitable VIP core materials is extremely important. Conventional barrier films of plastics materials, such as are described for example in
EP 0 517 026 A1, do not produce the necessary gas barrier effect. Although gas-absorbing substances or substances that react with gases ("getter") can of course be added to the core layer in order to trap gases that diffuse in and thereby maintain the low pressure in the VIP, this measure does not always prove satisfactory. For this reason an aluminium composite film is preferably used as a total gas barrier in order to maintain the vacuum in the VIP. This aluminium composite film however dissipates so much heat at the edges that a large part of the insulating effect of the VIPs is lost. Of course, this effect is detected only when measuring the thermal transmission in a complete refrigeration unit. The influence of the edge effects cannot be detected when measuring the coefficient of thermal conductivity according to DIN 18164 Parts 1 and 2.

Nevertheless, VIPs based on a core layer of plastics foams have achieved a significant market penetration since their dimensions can be accurately matched to requirements and they can be produced simply and inexpensively in the form of very flat (plane) sheets. However, the aforementioned disadvantage of heat transmission via the edges of the double-sided aluminium film restricts their further widespread use.

The object of the present invention was accordingly to provide VIPs that exhibit the advantages of VIPs based on a core layer of plastics foams, namely flat (plane) surfaces and dimensionally accurate processability, but avoid or substantially reduce the losses in insulating performance due to edge effects.

According to the invention this object was achieved by vacuum insulating panels (VIPs) having a microporous sheet as core layer and a covering of a highly gas diffusion impermeable plastics film comprising at least 7 layers having the following layer sequence

1. polyolefin heat-sealable layer (I)
2. adhesive or bonding layer (II)
3. gas barrier layer (III)
adhesive or bonding layer (II)

polyolefin layer (IV)

adhesive or bonding layer (II)

a layer (V) consisting substantially of polyester and/or polyamide and/or polypropylene sputtered with aluminium or SiOx or a metal oxide of the 2nd or 3rd main groups.

With a VIP according to the invention an oxygen diffusion of substantially below 0.01 cm$^3$/m$^2$ d bar and a water vapour diffusion of substantially less than 0.02 g/m$^2$ d can be achieved, with the result that the durability of the insulating effect of a VIP fabricated in this way corresponds to practical requirements. A loss of insulating performance due to edge effects, as occurs when using aluminium composite films according to the prior art, is not found.

Polyolefin homopolymers or polyolefin copolymers may be used as polyolefin heat-sealable layer (I). Preferred are linear low density polyethylene ("LLDPE"), polybutylene ("PB"), ethylvinyl acetate ("EVA"), high density polyethylene ("HDPE"), ionomers ("I") and mixtures of these substances. According to the invention a multi-layer embodiment of the polyolefin heat-sealable layer (I) produced by co-extrusion of a plurality of layers from the aforementioned materials is also possible. The thickness of the polyolefin heat-sealable layer (I) is preferably 20 to 200 μm, particularly preferably 50 to 100 μm.

As adhesive or bonding layer (II) there are preferably used commercially available adhesives such as in particular two-component polyurethane adhesives. Polyolefin adhesives, preferably of polyethylene homopolymers, ethylene/ethyl acrylate ("EAA") or ethylene/methacrylic acid ("EMMA") may however also be used. The thickness of the adhesive layer or bonding layer (II) is preferably at most 6 μm, particularly preferably 2 to 6 μm.

The gas barrier layer (III) preferably consists substantially of polyvinyl alcohol ("PVOH"), ethylene/vinyl alcohol copolymer ("EVOH") and/or of polyamide or of
mixtures of PA and EVOH or, in the case of a multi-layer embodiment, of a layer-type combination of PA and EVOH or of mixtures of PA and EVOH, and is preferably stretched at least monoaxially. The gas barrier layer is optionally provided with a barrier lacquer coating, preferably with an acrylic lacquer. The thickness of the gas barrier layer (III) is preferably 10 to 120 μm, and in the single-layer embodiment is particularly preferably 10 to 20 μm.

The polyolefin layer (IV) preferably consists substantially of polyethylene, polypropylene or polyethylene copolymers. According to the invention this layer is preferably 5-500 μm, particularly preferably 50-200 μm thick. It has been found in this connection that the relatively thick polyolefin layer (IV) imparts a substantially smoother and more uniform surface to the VIP. This is particularly advantageous in the bonding of the VIP when installing a refrigeration unit. In the case of a folded VIP the surface wetted with adhesive is generally not sufficient for an adhesion of the VIP.

The layer (V) of polyester and/or polyamide and/or polypropylene is preferably sputtered, on the side remote from the remaining layers, in a conventional manner with aluminium, SiOx or a metal oxide of the 2nd or 3rd main groups, and may optionally be provided on the non-sputtered side with a barrier layer lacquering, preferably with an acrylic lacquer. The layer (V) is preferably a layer consisting substantially of polyester or polypropylene that has been sputtered with aluminium, preferably in a thickness of 30 to 80 nm. The thickness of the layer (V) is preferably 10 to 40 μm, particularly preferably 10 to 20 μm.

The at least 7-layer plastics film that is also the subject of the present invention may contain in one or more layers, normal amounts of conventional additives and auxiliary agents such as for example lubricants, anti-blocking agents and antistatic agents.

It has been found that the unexpectedly high impermeability was achieved specifically by a combination of a relatively thick polyolefin layer (IV) together with
the gas barrier layer (III) preferably of polyvinyl alcohol, and the sputtered layer (V). It is also important in this connection that the gas barrier layer (III) in the overall structure is arranged directly underneath the heat-sealable layer and is thus protected from moisture.

According to the invention VIPs that employ plastics foams as core layer are preferred. The plastics foams may be polyurethane or polystyrene foams. Also suitable are sheets produced from ground and pressed plastics foams, such as described for example in EP 0791155 B 1.

As core layer there are preferably used according to the invention microcellular, open-pore foamed sheets, in particular of polyurethane or polystyrene. In a further preferred embodiment ground, closed-cell foamed materials that have optionally been compressed under the addition of suitable binders to form sheets, serve as core layer for the VIPs according to the invention. In this way the production of VIPs according to the invention can be incorporated in the recycling process for spent foams.

The production of the VIPs is normally carried out by placing the microporous sheet serving as core layer in a bag prefabricated from the films according to the invention (polyolefin/hot-sealable layer (I) on the inside) and sealing the still open edge in a vacuum of 10⁻³ to 1 torr. The VIP according to the invention is obtained after the aeration of the vacuum chamber.

The high gas impermeability of the film according to the invention imparts a sufficient durability to the VIP despite the low absorption capacity of the core layer. If nevertheless a getter is to be used in order to ensure durability of the VIP, the amount used may be correspondingly small. Also, even the use of small amounts of a substance that binds water vapour may possibly be sufficient. Examples of suitable getters are:
in order to bind the atmospheric constituents oxygen and nitrogen, alkali and alkaline earth metals; to bind moisture and carbon dioxide, alkaline earth oxides; and in order to bind just moisture, commercially available silica gels and molecular sieves. Suitably formulated getters made from these materials are commercially available.

The film according to the invention may in a special embodiment also be used only to produce one side of the film bag, the opposite side forming a conventional multi-layer film with an aluminium barrier layer, which preferably comprises an Al layer with a thickness of 6-20 µm and a PE layer with a thickness of 50-200 µm. In this embodiment too the thermal insulation is not significantly affected by edge effects.

The VIPs according to the invention may be widely used as high-performance insulating materials for insulation in building and construction, industrial insulation, and in particular in refrigeration equipment.

When used in refrigeration equipment the VIPs usually occupy part of the insulation volume - refrigeration equipment is normally insulated with rigid polyurethane foam. In this way energy savings of up to 30% can be achieved without increasing the wall thickness.
Examples:

**Measurement methods:**

5 The properties of the multi-layer film according to the present invention are determined according to the following methods:
The oxygen, nitrogen and carbon dioxide permeability of the films is determined according to DIN 53380.
The water vapour permeability of the films is determined according to DIN 53122.

10 The coefficient of thermal conductivity $\lambda$ is determined according to DIN 18164 Part 1 and Part 2.
The determination of the cabinet index (heat transmission through the shell of the refrigeration equipment) is described in detail in Example 7.

15 The subject of the invention will be described in more detail hereinafter with the aid of the following examples:

1. **Films:**

20 The high barrier effect of the films according to the invention was demonstrated using the following examples of films:

**Example a:**

25 Layer I: Polyolefin heat-sealable layer of ethylene/vinyl acetate copolymer, 3.5% vinyl acetate, 50 $\mu$m
Layer II: two-component polyurethane adhesive, 2 $\mu$m
Layer III: gas barrier layer of polyvinyl alcohol, biaxially stretched, 12 $\mu$m
Layer II: two-component polyurethane adhesive, 2 $\mu$m
Layer IV: polyethylene layer, 120 $\mu$m
Layer II: two-component polyurethane adhesive, 2 $\mu$m
Layer V: metallised biaxially stretched polyethylene terephthalate film, 12 $\mu$m
Example b:

Layer I: Polyolefin heat-sealable layer of ethylene/vinyl acetate copolymer, 3.5% vinyl acetate, 50 μm
5 Layer II: two-component polyurethane adhesive, 2 μm
Layer III: gas barrier layer of polyvinyl alcohol, biaxially stretched, 12 μm
Layer II: two-component polyurethane adhesive, 2 μm
Layer IV: polyethylene layer, 120 μm
Layer II: two-component polyurethane adhesive, 2 μm
10 Layer V: metallised biaxially stretched polypropylene film, 20 μm

Example c:

Layer I: Polyolefin heat-sealable layer of ethylene/vinyl acetate copolymer, 3.5% vinyl acetate, 50 μm
15 Layer II: two-component polyurethane adhesive, 2 μm
Layer III: gas barrier layer of a PVOH layer lacquered on both sides with PVDC
Layer II: two-component polyurethane adhesive, 2 μm
Layer IV: polyethylene layer, 120 μm
Layer II: two-component polyurethane adhesive, 2 μm
Layer V: metallised biaxially stretched polyethylene terephthalate film, 12 μm

Example d:

25 Layer I: Polyolefin heat-sealable layer of ethylene/vinyl acetate copolymer, 3.5% vinyl acetate, 50 μm
Layer II: two-component polyurethane adhesive, 2 μm
Layer III: gas barrier layer of a co-extruded PA/EVOH/PA layer
Layer II: two-component polyurethane adhesive, 2 μm
Layer IV: polyethylene layer, 120 μm
Layer II: two-component polyurethane adhesive, 2 μm
Layer V: metallised biaxially stretched polyethylene terephthalate film, 12 μm

Comparison example e: (Combithen PXX, according to EP 0 517 026 A1):

1st layer: polyolefin layer, 50 μm
2nd layer: two-component polyurethane adhesive, 2 μm
3rd layer: polyvinyl alcohol layer, 12 μm
4th layer: two-component polyurethane adhesive, 2 μm
5th layer: polyolefin layer, 120 μm
6th layer: two-component polyurethane adhesive, 2 μm
7th layer: polyvinyl alcohol layer, 12 μm
8th layer: two-component polyurethane adhesive, 2 μm
9th layer: polyolefin layer, 120 μm
10th layer: two-component polyurethane adhesive, 2 μm
11th layer: stretched polyethylene terephthalate film, 12 μm

Comparison example f: (Aluthen, P. Wolff-Walsrode):

1st layer: polyolefin layer, 50 μm
2nd layer: two-component polyurethane adhesive, 2 μm
3rd layer: stretched polyethylene terephthalate film, 12 μm
4th layer: two-component polyurethane adhesive, 2 μm
5th layer: aluminium film, 12 μm
6th layer: two-component polyurethane adhesive, 2 μm
7th layer: stretched polyethylene terephthalate film, 12 μm

The following water vapour, oxygen, nitrogen and carbon dioxide permeabilities were determined:
<table>
<thead>
<tr>
<th>Example</th>
<th>Permeability [cm³/m²·bar] (23°C, 0% rel. humidity)</th>
<th>Water Vapour Permeability [g/m²·d] (23°C, 85% rel. humidity)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O₂</td>
<td>N₂</td>
</tr>
<tr>
<td>a</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>b</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>c</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>d</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Comparison Example</td>
<td></td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>f</td>
<td>unmeasurably small</td>
<td>unmeasurably small</td>
</tr>
</tbody>
</table>

2.) Description of the film bag:

The film bag was produced by a three-sided welding process using 50 x 50 cm size pieces of film. Bags were produced from the following materials:

I. Symmetrically fabricated film bag of a commercially obtainable aluminium-containing multi-layer film (Aluthen-P from Wolff Walsrode, see Example 1.f).

II. Symmetrically fabricated film bag of a commercially obtainable metal-free barrier layer film (Combithen PXX from Wolff Walsrode, see Example 1.e).

III. Symmetrically fabricated film bag of the multi-layer film according to the invention and as disclosed in Example 1.a.

IV. Asymmetrically fabricated film bag of the multi-layer film according to the invention described in 2.III and the aluminium-containing multi-layer film described in 2.I.
3.) Description of the core layer – sheet of recycled rigid foam corresponding to WO 96/14207

1000 g of a PUR rigid foam flour from a refrigeration equipment recycling plant are uniformly mixed with 35 g of water and 100 g of a polyisocyanate mixture of diphenylmethane diisocyanates and polyphenyl-polymethylene-polyisocyanates (Desmodur® VP PU 1520 A20; Bayer AG) in a Lödige-Pflugschar mixer equipped with twin substance nozzles. A moulded part of size 400 x 400 mm is formed from this mixture in a mould frame, and is uniformly compacted and then compressed to 25 mm in a laboratory press under a pressure of 5 bar and at a temperature of 120°C for 8 minutes using a time-measurement program.

A porous 25 mm sheet having a bulk density of 250 kg/m³ is obtained. The sheet was heated for ca. 2 hours at 120°C in order to free it from all volatile constituents.

4. Production of VIPs

The panels produced in 3. were placed in the film bags produced according to 2.1 to 2.4, evacuated to a pressure of 2 x 10⁻¹ torr and welded. The corresponding VIPs are obtained after aeration.

It was found that the VIPs produced with the thick film according to the invention have a substantially smoother surface than those with a thin film.

The still existing, low water vapour permeability can be determined by measuring the weight increase of the VIPs after a storage test. The weight increase was determined after a storage time of 1 year and was extrapolated to 15 years. In this connection it was borne in mind that the core layer consisting of the rigid polyurethane foam has a water absorption capacity of about 0.5 to 1% of its own weight and for this reason the pressure in the panel does not initially rise. The weight increase on account of the oxygen, nitrogen and carbon dioxide permeability can be ignored in the comparison, since it fluctuates only in the milligram range.
Calculated and measured weight increases from the water vapour permeability:

<table>
<thead>
<tr>
<th>VIP of Film Bag</th>
<th>Weight Increase [g]</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>After 1 Year (calculated)</td>
<td>After 1 Year (measured)</td>
<td>Extrapolation to 15 Years</td>
</tr>
<tr>
<td>2.I</td>
<td>0</td>
<td>0.2</td>
<td>3</td>
</tr>
<tr>
<td>2.II</td>
<td>11.68</td>
<td>5.34</td>
<td>80.1</td>
</tr>
<tr>
<td>2.III</td>
<td>1.75</td>
<td>1.63</td>
<td>24.45</td>
</tr>
<tr>
<td>2.IV</td>
<td>0.88</td>
<td>0.72</td>
<td>10.8</td>
</tr>
</tbody>
</table>

5. **Measurement of the coefficient of thermal conductivity \( \lambda \)**

The thermal transmission was measured according to DIN 18164 Parts 1 and 2 for the VIPs with the film structure 2.I to 2.IV produced in 4. The sheets all have a comparable thermal transmission of 9.0-9.1 mW/m²K.

6. **Incorporation of VIPs in a refrigerator**

As shown in a vertical section in Fig. 1, VIPs (reference numeral (1)) with the film structure according to 2.I to 2.IV, but with dimensions of 60 x 50 x 2.5 and 50 x 50 x 2.05, were bonded together before installation on the inside of the external housing (reference number 2)) in a table-top refrigerator. A further VIP was bonded to the inside of the door and to the rear wall (both not shown in Fig. 1). The VIPs thus occupied part of the insulation volume. After the installation of the internal housing (reference numeral 3)) the remaining insulation volume was conventionally filled with PUR foam (reference numeral 4)).

Four refrigerators having different film structures of the VIPs employed in each case were produced.
After bonding, the VIPs formed with the preferred thick film according to the invention had bonded better and more permanently than VIPs produced with thin films, such as for example according to the structure 2.I. In the latter case, after the foaming of the residual spatial volume, in some cases there was a lack of bonding between the VIP and the outer covering.

7. Measurement of the cabinet index of refrigerators produced with different VIPs

The refrigerators produced under 6. were investigated as regards their cabinet indices as follows: by means of an adjustable electric heating device installed in the interior of the refrigerator, the interior space was raised to a temperature 30°C to 40°C higher than the ambient temperature. After the internal temperature had reached a stationary state (as a rule after 4 days), the cabinet index Z (in W/K) was determined by measuring the electrical heating effect and the mean temperature difference between the interior and surroundings over a period of 24 hours, the temperature measurements in the interior being made using a total of 6 thermocouples. The following results were obtained:

<table>
<thead>
<tr>
<th>Film Structure of the VIP</th>
<th>Cabinet Index (W/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.I</td>
<td>0.36</td>
</tr>
<tr>
<td>2.II</td>
<td>0.30</td>
</tr>
<tr>
<td>2.III</td>
<td>0.29</td>
</tr>
<tr>
<td>2.IV</td>
<td>0.29</td>
</tr>
</tbody>
</table>

As can be seen, in the case of 2.I (aluminium composite film on both sides) the thermal transmission is substantially greater than when using the plastics film, and what is more even when the plastics film is used only on one side in combination with an aluminium composite film (2.IV) on the other side.
Patent Claims

1. Vacuum insulation panels (VIPs), having a microporous sheet as core layer and a covering of a plastics film comprising at least 7 layers in the layer sequence

   (1) polyolefin heat-sealable layer (I)
   (2) adhesive or bonding layer (II)
   (3) gas barrier layer (III)
   (4) adhesive or bonding layer (II)
   (5) polyolefin layer (IV)
   (6) adhesive or bonding layer (II)
   (7) a layer (V) consisting substantially of polyester and/or polyamide and/or polypropylene sputtered with aluminium or SiOx or a metal oxide of the 2nd or 3rd main groups.

2. Vacuum insulation panels (VIPs) according to claim 1, wherein the polyolefin heat-sealable layer (I) is a single-layer or multi-layer film and consists substantially of polyolefin homopolymers or polyolefin copolymers.

3. Vacuum insulation panels (VIPs) according to claim 1 or 2, wherein two-component polyurethane adhesives or polyolefin adhesives are used as adhesive layer or bonding layer (II).

4. Vacuum insulation panels (VIPs) according to any one of claims 1 to 3, wherein the gas barrier layer (III) may be formed substantially of polyvinyl alcohol ("PVOH"), ethylene/vinyl alcohol copolymer ("EVOH") and/or of polyamide or of mixtures of PA and EVOH, and may optionally be multi-layer in structure.

5. Vacuum insulation panels (VIPs) according to any one of claims 1 to 4, wherein the polyolefin layer (IV) consists substantially of polyethylene,
polypropylene or polyethylene copolymers, and preferably has a thickness of 5-500 µm.

6. Vacuum insulation panels (VIPs) according to any one of claims 1 to 5, wherein the layer (V) is a layer consisting substantially of polyester or polypropylene that has been sputtered with aluminium, preferably in a thickness of 30 to 80 nm.

7. Vacuum insulation panels (VIPs) according to any one of claims 1 to 6, wherein as core layer there are used according to the invention microcellular, open-pore foam sheets of polyurethane or polystyrene.

8. Vacuum insulation panels (VIPs) according to any one of claims 1 to 6, wherein ground closed-cell foams that have optionally been compressed with the addition of suitable binders into sheets serve as core layer.

9. Vacuum insulation panels (VIPs) according to any one of claims 1 to 8, wherein only one side of the covering has a plastics film comprising at least 7 layers in the layer sequence

(1) polyolefin heat-sealable layer (I)
(2) adhesive or bonding layer (II)
(3) gas barrier layer (III)
(4) adhesive or bonding layer (II)
(5) polyolefin layer (IV)
(6) adhesive or bonding layer (II)
(7) a layer (V) consisting substantially of polyester and/or polyamide and/or polypropylene sputtered with aluminium or SiOx or a metal oxide of the 2nd or 3rd main groups.

and the opposite side is formed by a conventional multi-layer film with an aluminium barrier layer.
10. Plastics film for producing vacuum insulation panels (VIPs) of at least 7 layers in the layer sequence

5  (1) polyolefin heat-sealable layer (I)
    (2) adhesive or bonding layer (II)
    (3) gas barrier layer (III)
    (4) adhesive or bonding layer (II)
    (5) polyolefin layer (IV)

10  (6) adhesive or bonding layer (II)
    (7) a layer (V) consisting substantially of polyester and/or polyamide and/or polypropylene sputtered with aluminium or SiOx or a metal oxide of the 2\textsuperscript{nd} or 3\textsuperscript{rd} main groups.

15  11. Use of a vacuum insulation panel (VIP) according to any one of claims 1 to 9 for insulating refrigeration equipment.