CONVENTION APPLICATION FOR A PATENT

We, N.V. PHILIPS' GLOELAMPENFABRIEKEN, a limited liability company, organized under the laws of the Kingdom of The Netherlands and carrying on business at 29 Emraasingel, Eindhoven, The Netherlands, hereby apply for the grant of a Patent for an invention entitled:

"Method of producing a composite body".

which is described in the accompanying complete specification. This application is made under the provisions of Part XVI of the Patents Act 1952 - 1969 and is based on the following application or applications for a patent or patents or similar protection made in the following country or countries on the following date or dates:

in The Netherlands, Appln. No. 7610126, filed 13th September 1976
in , Appln. No. , filed
in , Appln. No. , filed

Our address for service is: Messrs. PHILLIPS, ORMONDE AND FITZPATRICK Patent Attorneys, 37-41 Queen Street, Melbourne 3000, Australia.

Dated this 18th August 1977

N.V. PHILIPS' GLOELAMPENFABRIEKEN

To: THE COMMISSIONER OF PATENTS
CCMONWEALTH OF AUSTRALIA

Patents Act

DECLARATION FOR A PATENT APPLICATION

In support of the (a) application made by N.V.Philips’Gloeilampenfabrieken, 

(b) (hereinafter called "applicant(s)") for a patent 

(c) 

(d) 

"Method of producing a composite body".

In World Intellectual Property Organization (WIPO) Application No(s).  

(a) 

(b) 

(c) 

(d) 

(f) 

(g) 

(h) 

(i) 

(See headnote.)

(See headnote.)

Declared at Eindhoven, The Netherlands 18th August 1977

To: The commissioner of Patents
A method of producing a composite body of which at least one of the parts consists of metal and, possibly, one of glass, in accordance with which the parts are bonded by means of a thermoplastic material, characterized in that the parts, of which as regards the metal a surface layer is converted into a coherent and properly adhering oxide layer and, possibly, the parts of oxidic glass, of which at least a surface layer not more than 300Å thick has a composition with a deficiency in lattice-forming id/or lattice-modifying ions relative to oxygen ions are bonded by means of a film of polyethylene whose surface is modified by treating it with an oxidant, at a temperature between 125 and 250°C and a pressure of at least 56/\text{mm}^2.
APPLICANT'S REF: PHILIPS ORMONDE & FITZPATRICK

Applicant(s): PHILIPS ORMONDE & FITZPATRICK

Address(es) of Applicant(s): 37-41 Queen Street

Actual Inventor(s):

Address for Service is: P.O. Box 600, Melbourne, Australia, 3000

Complete Specification for the invention entitled:

"Method for producing a composite body"

The following statement is a full description of this invention, including the best method of performing it known to applicant(s):
"Method of producing a composite body."

The invention relates to a method of producing a composite body of which at least one of the parts consists of metal and to the body thus obtained.

In particular it relates here to a composite body which consists of metal parts which are bonded together or to a body in which a metal part is bonded to a glass part.

United Kingdom Patent Specification 931,416 discloses such a composite body which consists of metal parts or of a combination of metal parts and glass parts and a thermoplastic material disposed therebetween, such as polyethylene, which fuses the parts together.

The method of producing this composite body consists in that a dispersion of particles of the thermoplastic material is prepared; the surfaces to be fused are coated, thereafter heated until the thermoplastic material melts, the coated surfaces of the parts are brought into contact with one another, heated again to re-fuse and thereafter cooled.

This method is rather cumbersome and, in addition, it can only be used if the requirements imposed on the bond are not too high.
By means of the method according to the invention the parts are bonded together in a much simpler manner by means of a film of thermoplastic material having a thickness of between 5 and 100 \( \mu \text{m} \) in such a way that very high requirements may be imposed on the bond. Also the chemical resistance of the bond is of a very high quality. Depending on the kind of material it withstands a life test of 200 hours in water of 100\(^\circ\)C.

In accordance with the invention the parts of which at least one consists of metal and of which metal at least a surface layer is converted into a coherent and properly adhering oxide layer and, possibly, parts of oxidic glass of which at least one surface layer of a thickness of not more than 300\( \AA \) has a composition with a deficiency of lattice forming and/or lattice modifying ions relative to oxygen ions, are bonded by means of a film of polyethylene whose surface area is modified by treating it with an oxidant, at a temperature between 125 and 250\(^\circ\)C and a pressure of at least 5 g/\( \text{mm}^2 \).

Of prime importance is the oxidative pretreatment of the polyethylene film, without which a proper fusion cannot be obtained.

In addition it is necessary that the metal has a coherent and properly fusing oxidic surface layer. Many metals, such as aluminium and stainless
steel kinds furnish a reasonable bond. An additional treatment such as a thermal oxidation treatment or electrolytic oxidation results in many cases in a considerable improvement of the bond quality.

For performing the method according to the invention in accordance with which a metal part must be bonded to a glass part the following should be taken in consideration as regards the glass surface,

It appeared that glasses having a high content of lattice forming oxides \( \text{SiO}_2, \text{B}_2\text{O}_3, \text{Al}_2\text{O}_3 \) of more than approximately 80 mole % have naturally already a surface layer with a deficiency in lattice-modifying ions relative to the oxygen ions compared to the mass of the relevant glass part. It appeared that this type of glasses, for example quartz glass and other hard glasses, for example of the borosilicate type, appeared to enable bonding by means of superficially modified polyethylene to a metal part without further measures. In the glass part the atomic share of metals in the surface layer is approximately half of that in the mass. The surface area in which the deficiency occurs is only some dozens of Å thick and this deficiency decreases from the outside towards the inside.

In glasses, such as soda lime glass which contain a large proportion of alkali metal oxides and
alkaline earth metal oxides, such a metal deficiency does not occur. Therefore these glasses cannot be bonded without treatment by means of polyethylene film to a metal part. However, in accordance with measures which are known per se a metal deficiency can be effected in a surface layer also in this type of glasses. By such measures, such as treating the glass part with a strong alkali metal hydroxide solution (pH > 10) and by thereafter exchanging metal for H⁺ by contact with a solution of an acid or a treatment consisting of keeping the glass part for some time into contact with moist sulphur dioxide-containing air (DTPS 1,156,946) the parts can be bonded by means of superficially modified polyethylene in accordance with the invention to a metal part.

In accordance with a further improvement of the invented method the surface of the pretreated polyethylene and/or glass surface with metal deficiency is treated with a silane by hydrolysing this compound of, for example, the structure

\[ R Si X_3 \]

wherein

\[ R = -(CH_2)_3-NH_2, -(CH_3)_2-C-CH_2 \]

and X is halogen or OR', wherein R' = alkyl, preferably methyl, ethyl or propyl, in water, onto the glass surface or into the gas phase. Then compounds are obtained of the type \( R Si X (3-n) (OH)_n \), wherein
n = 1, 2 or 3, which effect a still stabler bond between the glass and the polyethylene. This results in a pronounced prolongation of the life of the composite body, especially in a humid environment.

By means of modern physical methods of analysis, for example secondary ions mass spectros- copy (SIMS), it is possible to determine the composition of the glass in a surface layer of only a few dozens of Å. By way of illustration the results of the analysis of two types of glass, namely a borosilicate glass of the composition expressed by weight:

1) \( \begin{align*}
SiO_2 & \quad 78.9 \\
B_2O_3 & \quad 14.4 \\
Na_2O & \quad 3.5 \\
K_2O & \quad 1.2 \\
MgO & \quad 0.3 \\
Al_2O_3 & \quad 1.7
\end{align*} \)

and a soda lime glass having a composition expressed in percent by weight:

2) \( \begin{align*}
SiO_2 & \quad 68.0 \\
Na_2O & \quad 16.8 \\
K_2O & \quad 1.0 \\
MgO & \quad 3.9 \\
BaO & \quad 2.0 \\
Al_2O_3 & \quad 2.6 \\
CaO & \quad 5.7
\end{align*} \)

The following analyses were made thereof:

a) of a cross-section in the mass of the glass;

b) of the surface at a depth of approximately 50 Å;

c) of the surface after having been treated for 1 hour in 1 N KOH at 50°C;

d) of the surface after having been treated for 1
hour in a mixture at 60°C of 1:1:2, in parts by volume, HNO₃ (d = 1.43) H₂SO₄ (d = 1.84) and water.

TABLE
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Polyethylene exists in several varieties, depending on the degree of polymerisation and the manner of polymerisation, that is to say predominantly in the form of chains or with pronounced branches of all kinds of intermediate forms. For the customary processes a distinction is made between the "low pressure process" and the "high pressure process", which approximately results in products having a high density and products having a low density respectively. Tests within the scope of the invention proved that those varieties are equivalent in this respect.

The method according to the invention can be used for bonding prism blocks to metal base plates, fastening lenses or lens systems in metal envelopes, which results at the same time in bonding and sealing, and for fabricating capacitor microphones in which the polyethylene performs the combined function of insulation, fastening and spacing.

To explain the invention some examples will now be described.

Example 1:

Two brass plates were degreased in acetone and oxidized by heating them for 20 minutes in air at a temperature of 400°C.

Polyethylene film, 20/μm thick was degreased by contact with acetone of 20°C for 3 minutes, thereafter rinsed in water and dried. There-
after the film was kept into contact for 5 minutes with a solution of 60°C containing 52 % by weight of H₂SO₄, 6 % by weight of sodium-bichromate and 42 % by weight of water and dried.

The two brass plates between which the film was disposed were kept at a pressure of 1.4 kg/cm² for 8 minutes at 160°C.

The tangential shearing force, determined at 25 °C amounted to 107 kg/cm of adhering surface.

After a lifetest of 50 hours in water of 100°C the bond was still intact; the shearing force mentioned above was 97 kg/cm².

If non-pre-treated brass is used in the method described above then the band fails during the lifetests already within 10 hours in water of 100°C. If the polyethylene film, after the oxiditive treatment is treated for 1 minute at 60°C in a solution of 85 % by weight of H₂SO₄, 2.5 % by weight of K₂Cr₂O₇ and 12.5 % by weight of H₂O for 5 minutes in a 0.2 solution of the silane NH₂(CH₂)₃Si(OC₂H₅)₃ of Union Carbide in water then the shearing force is 97 kg/cm² and after a life test of 50 hours in water of 100°C is 95 kg/cm².

Example 2:

Degreased aluminium plates were anodically oxidized in known manner (for example in H₂SO₄ - H₃PO₄ solution). A 15 µm thick oxide layer was
formed. The plates between which polyethylene film, which had been treated as in example 1 was disposed were kept for 5 minutes under a pressure of 1.4 kg/cm² and at a temperature of 160°C. The tangential shearing force, determined at 25°C was 170 kg/cm² of adhering surface. After 50 hours the above defined shearing forces still amounted to 130 kg/cm². After a life test of 200 hours in water of 100°C the bond was still intact. Non-oxidized aluminium withstood this life-test for only 110 hours.

**Example 3:**

Plates of 2 kinds of Cr-Ni-steel, (namely N 544: Cr 25 Ni 20 and N 129: Cr 18 Ni 8 respectively) were degreased and each bonded to a glass plate by means of a polyethylene film in the manner described in example 1. An oxidation treatment of the metal is not required because the natural oxide skin is already sufficient. After having been exposed for 200 hours to the above described life test the bond remained intact. Immediately after making the bond the shearing force amounted to 156 and 129 kg/cm² respectively.

**Example 4:**

A die-cast base plate of an aluminium-silicon-alloy containing approximately 11% by weight of Si was coated with an oxide layer in the following manners,
a) by anodic oxidation in oxalic acid in the customary manner, described in the literature
b) as described in paragraph (a) above, and thereafter kept for 10 minutes in boiling demineralised water.

A glass prism system consisting of glass having the composition expressed in percent by weight

\[
\begin{align*}
\text{SiO}_2 & : 69.0 \\
\text{B}_2\text{O}_3 & : 10.0 \\
\text{Na}_2\text{O} & : 9.0 \\
\text{K}_2\text{O} & : 8.3 \\
\text{BaO} & : 3.4 \\
\text{As}_2\text{O}_3 & : 0.3
\end{align*}
\]

was pressed, after degreasing in 1 N KOH of 60°C for 1 hour and drying, a 50/µm thick polyethylene film (low density) being inserted, at a pressure of 1.2 kg/cm² for 8 minutes at 160°C unto the aluminium plate.

A bond was obtained, the tangential shearing force of which was 110 and 113 kg/cm² respectively.

After treating the film with the silane in the manner described in example 1 the shearing force was 76 kg/cm².
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS

1. A method of producing a composite body of which at least one of the parts consists of metal and, possibly, one of glass, in accordance with which the parts are bonded by means of a thermoplastic material, characterized in that the parts, of which as regards the metal a surface layer is converted into a coherent and properly adhering oxide layer and, possibly, the parts of oxidic glass, of which at least a surface layer not more than 300Å thick has a composition with a deficiency in lattice-forming and/or lattice-modifying ions relative to oxygen ions are bonded by means of a film of polyethylene whose surface is modified by treating it with an oxidant, at a temperature between 125 and 250°C and a pressure of at least 5 g/mm².

2. A method as claimed in claim 1, characterized in that the deficiency is effected by hydrolysing the parts consisting of glass having a high alkali content in an aqueous solution of an alkali metal hydroxide and the exchanging the lattice-forming and lattice-modifying ions at the surface for hydrogen ions by treating with a solution of one or more acids.

3. A method as claimed in claim 1, charac-
characterized in that the parts consisting of glass with a higher Na$_2$O content Na$^+$-ions are extracted in a surface layer in a manner known per se by treating it with a moist SO$_2$-atmosphere and rinsing with water.

4. A method as claimed in claim 1, 2 or 3, characterized in that the pretreated polyethylene film or the glass are furthermore treated with a silane.

5. Objects obtained in accordance with the method described in any one of claims 1 - 4,

DATED: 30th August, 1977

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