

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
16 April 2009 (16.04.2009)

PCT

(10) International Publication Number
WO 2009/046725 A1

(51) International Patent Classification:
B32B 7/02 (2006.01) **C09D 4/00** (2006.01)
C08J 7/00 (2006.01)

(21) International Application Number:
PCT/DK2008/050246

(22) International Filing Date: 6 October 2008 (06.10.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PA 2007 01476 12 October 2007 (12.10.2007) DK

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(54) Title: A METHOD OF PRODUCING AN ITEM AND AN OVERMOLDED ITEM

(57) Abstract: The invention relates to a method of producing an item comprising providing a substrate, treating at least a surface section of said substrate by applying at least one primer layer, the total thickness of the at least one primer layer being up to 200 nm; and overmolding an elastomer onto and/or into the primer treated substrate. The item produced according to the invention comprises a very strong interfacial bonding between the substrate and the overmolded layer. The substrate and the elastomer form a very strong and durable bonding to each other, even when the materials differs in hardness and/or stiffness. The method can be used with silicone as overmolded elastomer.

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A METHOD OF PRODUCING AN ITEM AND AN OVERMOLDED ITEM

5 TECHNICAL FIELD

The present invention relates to a method of producing an item comprising an elastomer, such as silicone rubber applied onto a substrate and an item.

BACKGROUND ART

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A large number of prior art documents describe different methods of applying and bonding elastomers, such as silicone rubber, onto a substrate.

According to prior art methods, bonding of an elastomer to a substrate may be created by one or more of the following general methods:

15

a) Adding a primer comprising an organic chemical compound onto the substrate surface (e.g. a silane, titanium or zirconium coupling agents). The chemical compound has two types of functional groups, one type that is able to bond to the substrate and one type that is able to bond to the elastomer

20

b) Surface activation by physical vapour deposition, chemical vapour deposition, plasma activation often followed by applying a primer
c) Chemical modification of the elastomer (self-bonding compounds) that is able to bond directly to the substrate surface.

25

US 5,378,535 describes a primer system for silicone elastomers bonded to glass or plastic substrates. The primer system is a two-layer system consisting of a first thin layer of a silica-based adhesion promoter which is applied to the substrate using PVD, CVD, evaporation or sputtering, and a second layer of an organosilane comprising silanol, and (ii) polymerizable alkene and/or silicon hydride functional groups applied by wet chemical methods.

30

Even though it is mentioned that the second layer may be from 0.1 to about 5 microns in thickness, it will in practice be impossible to apply a layer with a thickness below 1 micron

- 5 In general it is not desirable to use wet chemistry which causes undesired waste. The coupling agents used in wet chemistry processed are often unstable and may hydrolyze in air and furthermore the bonding between coupling agent and substrate is often weak.
- 10 EP 781 823 relates to a primer composition comprising an organic silicon compound. The primer composition can be used to prime a substrate for promoting adhesion of silicone rubber to the substrate.
- 15 US 6,034,174 relates to a primer composition for incorporating into an addition curable polysiloxane resin and comprising an epoxy functional silane and an acid. The addition curable polysiloxane resin is self-adhesive when cured on top of a substrate. Other compositions of addition curable silicone compositions are disclosed in US 6,489,031 and US 5,085,894.
- 20 Chemical modification including the addition of organic primer compositions to addition curable silicone compositions leads to expensive raw materials, which only can be used for very specific applications and substrates. The handling is difficult and special tools are needed (as the elastomer bonds to the mould as well as to the substrate). The self bonding elastomers do not
- 25 bond to any kind of substrate.

DISCLOSURE OF INVENTION

- 30 The object of the invention is to provide a novel method of producing an item comprising a substrate and an elastomer, which method is simple and provides an item with a strong bonding between the substrate and the elastomer.

Another object of the invention is to provide a novel item comprises an elastomer and a substrate which are bonded to each other with a strong bonding.

- 5 These objects have been achieved by the invention as defined in the claims and described hereinafter.

The invention and embodiments thereof have several additional benefits which will be clear from the following description.

10

It should be emphasized that the term “comprises/comprising” when used in this specification is taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other stated features, integers, steps, components or groups thereof.

15

The term “overmolding” means herein to apply an elastomer or a precursor therefore to a substrate and cure the elastomer in contact with the substrate to bond the elastomer to the substrate. The term “overmolded elastomer” means an elastomer, which has been applied to a substrate e.g. in the form of a precursor, and cured in contact with said substrate. The term “overmolded item” means the item comprising the overmolded elastomer and the substrate.

20

- 25 The method of the invention comprises

- providing a substrate,
- treating at least a surface section of said substrate by applying at least one primer layer, the total thickness of the at least one primer layer being up to 200 nm; and
- 30 • overmolding an elastomer onto and/or into said primer treated substrate.

35

By the method of the invention it has thus been found that the substrate and the elastomer forms a very strong and durable bonding to each other, even when the materials differs in hardness and/or stiffness.

Furthermore the method is simple and fast and may be used on most any substrate.

- 5 The method of the invention has thus opened up for the production of completely new quality products, in particular products mainly composed of an elastomer and a non-elastomer.

Preferably the elastomer is overmolded onto the primer treated substrate.

10

In one embodiment the elastomer is overmolded onto the primer treated substrate and simultaneously at least partly into at least a part of the substrate, e.g. such as into a surface layer of the substrate where the surface layer e.g. have a thickness of 1 μm to 10 mm, such as 10 μm to 5
15 mm. The thickness of the surface layer of the substrate depends largely of the porosity of the substrate.

In one embodiment the substrate is at least partly porous, e.g. in the form of a porous polymer or in the form of a woven or a non-woven fabric, and the
20 method comprises overmolding the elastomer into at least a part of said substrate.

The overmolding of the elastomer into the substrate may e.g. include incorporating precursor(s) for the elastomer into the substrate using
25 overpressure and/or liquid/supercritical CO_2 treatment as described in any one of applicants copending applications US 2006/0148985, DK PA 2006 01439 and DK PA 2006 01440 followed by cross-linking (curing) to provide the elastomer.

- 30 The substrate may in principle be any kind of substrate of any material and with any shape. The substrate may be of a single material or it may be composed of two or more materials which may be composed in a homogenous fashion or an inhomogeneous fashion.

In one embodiment the substrate is of a material which is harder than the overmolded elastomer.

The substrate should preferably be a solid substrate at 20 °C and 1 atms.

5

In one embodiment the substrate is a non-elastomer.

In one embodiment the substrate is a polymer or a combination of different polymers. Examples of preferred polymers includes polymers selected from
10 the group consisting polyethylene (PE) polypropylene (PP), polycarbonate (PC), polyamide (PA), poly(phenylene sulphide) (PPS), polymethylmethacrylate (PMMA), polystyrene (PS), polyethyleneterephthalate (PET), and fluoropolymers.

15 In one embodiment the substrate is one or more of carbon and aramide, preferably in the form of fibers or particles, such as fibers with an average diameter of 1-100 μm and/or fibers/particles with a BET surface area of from 100 to 1500 m^2/g . Fibers comprising an overmolded elastomer may be used e.g. as fillers, in yarns and in other fiber based products.

20

In one embodiment the substrate is as mentioned above a porous material.

In one embodiment the substrate is a non woven fabric made of polymer fibres. The elastomer may e.g. be applied in order to be impregnated into an
25 outer layer of the fabric to provide membrane or barrier properties. Thereby a very strong membrane with pre-selected characteristics can be obtained.

In one embodiment the substrate is glass or a glass composition. An overmolded item comprising glass and an elastomer may be constructed to
30 have a unique combination of desired properties, such as a combination of strength, low permeability and relatively low hardness.

In one embodiment the substrate is a metal, such as iron, steel (stainless, duplex and other), aluminium and magnesium. In this embodiment the

elastomer may e.g. be applied in order to protect the metal against corrosion, to provide an electrically insulation or for other reasons.

5 In one embodiment the substrate is a ceramic material, such as oxide based ceramic materials, (alumina, zirconia), non-oxide based ceramic materials, (carbides, borides, nitrides, silicides).

In one embodiment the substrate is a composite of two or more of the above mentioned materials.

10

The substrate may have essentially plane surfaces or it may have a more curved shape.

15 The substrate may be in the form of particles and/or fibers irrespectively of the material e.g. fibers with an average diameter of 1-100 μm and/or fibers/particles with a BET surface area of 100 to 1500 m^2/g . The fibre substrate may e.g. be of glass.

20 In one embodiment the substrate is a film, having an essentially even thickness, preferably of 2 mm or less, such as 1 mm or less, such as 0.5 mm or less, such as 0.1 mm or less, such as 0.05 mm or less.

In one embodiment the substrate is a non-porous film.

25 In one embodiment the substrate is a porous film

In one embodiment the substrate has at least one thickness larger than 0.5 mm, the item preferably has a non-plane surface section, such as a curved and/or edged surface section.

30

In one embodiment the substrate is essentially nonflexible, and preferably has an inherent stiffness of at least 100, such as between 103 and 1010 N/m, such as between 104 and 106 N/m. The inherent stiffness may e.g. be measured using ASTM D 882.

35

The method of the invention comprises applying one or more primer layers where the total thickness of the primer layer(s) is up to 200 nm. It has been found that even thinner layer(s) of primer provide an even better result. It is therefore preferred that the total thickness of the at least one primer layer
5 being in the interval between 1 and 150 nm, such as between 5 and 100 nm, such as between 10 and 70 nm.

When referred to 'the primer layer' in the following it should be interpreted to mean at least one primer layer and the term may though be interpreted to
10 include one, two or several primer layers provided that the total thickness is not above 200 nm.

The primer layer should as mentioned be rather thin, namely about 200 nm or less in thickness. The inventors of the present invention has thus found
15 that by providing the primer layer as a rather thin layer a very strong bonding between the overmolded elastomer and the substrate can be obtained. In one embodiment the primer layer is applied using vapour deposition. A preferred method of applying the primer layer is by using plasma deposition of at least one monomer, the plasma preferably being a low (lower than
20 atmosphere) pressure AC (alternating current) or DC (direct current) plasma, wherein the pressure in the plasma during deposition treatment preferably being is 50 Pa or below, below 35 Pa, such as between 1 and 30 Pa.

By using plasma deposition for applying the primer a strong bonding
25 between the primer layer and the substrate can be obtained.

In one embodiment the primer layer being applied using plasma deposition. In principle any kind of plasma generating method may be used, but in order not to damage the substrate surface and/or the primer it is desired to use a
30 relatively low power plasma. In one embodiment the plasma being a low power plasma, preferably the applied power being 100 W/l plasma reactor or less, such as 50 W/l plasma reactor or less, such as 30 W/l plasma reactor or less, such as 20 W/l plasma reactor or less, such as 10 W/l plasma reactor or even less, such as 5 W/l plasma reactor or less, such as 3 W/l or

less, such as 1 W/l or even less. The volume of the plasma reactor is the volume in which the plasma is generated.

- 5 In one embodiment the primer layer being applied using plasma deposition where the plasma being a one phase plasma (one electrode or electrode group having same voltage and one grounded electrode/electrode group) preferably operating at a frequency of 50 Hz to 15 MHz, such as to 13.6 MHz.
- 10 In one embodiment the primer layer being applied using plasma deposition where the plasma being a two or multi phase plasma (two or more electrode or electrode groups each group having same voltage) preferably operating at a frequency of 50 Hz to 15 MHz, such as to 13.6 MHz.
- 15 The plasma deposition may preferably be performed at atmospheric pressure or a reduced pressure. Preferably the plasma deposition is performed at a low pressure, such as a pressure of 100 Pa or below, such as 50 Pa or below, such as 15 Pa or below.
- 20 In one embodiment the primer layer being applied using plasma deposition and the plasma deposition comprising applying the substrate in a plasma reactor, reducing the pressure in the plasma reactor, feeding the at least one monomer to the plasma reactor preferably together with a support gas selected from the group consisting of inert gases, oxidizing gasses or
- 25 reducing gasses, the support gas preferably being selected from the group consisting of N₂O, Ar, O₂, H₂, N₂ and mixtures thereof.

- The monomer or monomers in the form of gas may preferably feed into the reaction chamber in an amount of between 0.1 and 10 ml/min/l plasma
- 30 reactor. The deposition may e.g. be performed at any temperature but it is preferred that the deposition in the plasma reactor is performed at room temperature or at elevated temperature, more preferably at 15 - 100 °C.

The time for deposition depends largely on the deposition condition and the concentration of monomers. As example a deposition time of least 1 to 120 minutes may be used. Normally the deposition time will be 5-40 minutes

- 5 In one embodiment the at least one monomer being selected such that the deposited layer being essentially inorganic. In situations where both the substrate and the elastomer is of inorganic nature it is in particular preferred that the deposited layer being essentially inorganic
- 10 In one embodiment the at least one monomer being selected such that the deposited layer being organic. In situations where at least one of the substrate and the elastomer is of organic nature it is in particular preferred that the deposited layer being organic.
- 15 The one or more monomer(s) may preferably be selected in dependence on the type of substrate and the type of elastomer and its chemical curing (cross linking) reaction.

In one embodiment the at least one monomer comprises a Si containing monomer, preferably selected from the group consisting of silanes and/or organosilicon compositions such as hexamethyldisiloxane, methoxytrimethylsilane, tetramethoxysilane, hexamethylcyclotrisiloxane, methyltriethoxysilane, or phenyltriethoxysilane.

- 20
- 25 In one embodiment the one or more monomers comprising at least one monomer selected from silane, hexamethyldisiloxane, tetramethoxyxilane, tetraethoxysilane, the monomer being fed into the reaction chamber together with an oxidating composition such as O₂.
- 30 In one embodiment the plasma deposition comprises, feeding the at least one monomer to the plasma reactor together with a support gas. The support gas may preferably comprise an inert gas component and/or an oxidizing gas component. The inert gas may in principle be any kind of gas, but for economically and safety reasons Ar gas is preferred. Other useful inert
- 35 gasses include helium, neon and krypton. The oxidizing gas component may

preferably be O₂ or N₂O. The monomer(s) may preferably be selected to form a glass layer in the form of an oxide network including Si atoms. In one embodiment the Si based glass layer is provided using the method of applying a glass-barrier layer as described in WO07062665.

5

In one embodiment O₂ being fed to the reaction chamber in a molar ratio monomer: O₂ of from 20:1 to 1:20, such as from 10:1 to 1:10, such as from 5:1 to 1:5, such as from 2:1 to 1:2, such as about 1:1.

10 In one embodiment Ar being fed to the reaction chamber in a molar ratio monomer: Ar of from 10:1 to 1:10, such as from 5:1 to 1:5, such as from 3:1 to 1:3, such as from 2:1 to 1:2, such as about 1:1.

In one embodiment the one or more monomers comprising at least one
15 monomer selected from hexamethylsiloxane, tetramethoxysilane and tetraethoxysilane.

The primer layer may be essentially homogenous or its composition may vary. In one embodiment the method of the invention comprises applying a
20 graduated primer layer, the method comprising feeding at least two monomers in amounts which are varied relative to each other during the deposition treatment.

In one embodiment the method of the invention comprises applying one
25 single primer layer only. This single primer layer may be essentially homogenous or its composition may vary gradually along the thickness of the primer layer.

In one embodiment the method of the invention comprises applying two or
30 more primer layers. Each of these two or more primer layers may be essentially homogenous or its composition may vary gradually along the thickness of the primer layer.

In one embodiment comprising two primer layers, at least one of the primer
35 layers is a glass layer in the form of an oxide network including Si atoms,

preferably all primer layers are in the form of glass layers comprising an oxide network including Si atoms. The method may preferably comprise comprising applying alternating Si-oxide network and Si-C-oxide network layers, wherein the layers independently of each other optionally comprise
5 up to 50 % by atom mol of the respective layer composition of carbon.

In one embodiment where the method comprises applying two or more primer layers the method comprising

- 10 • applying a first primer layer comprising feeding one or more of the monomers selected from the group of siloxanes;
- applying a second primer layer onto the first primer layer comprising feeding one or more of the monomers selected from the group of alkanes, alkenes, alkynes, alcohols, amines, ammonia compounds with vinyl and/or allyl groups, compounds with ester and/or acid
15 groups and compounds with fluoro groups.

The two or more primer layers being applied immediately after each other in same plasma treating process.

20

Prior to applying the primer layer the substrate or at least the surface segment of the substrate may preferably be subjected to a pre-treatment e.g. for cleaning the surface and/or for activating the surface.

25 In one embodiment the method comprising pre-treating the surface segment of the substrate using plasma treatment prior to applying the primer layer.

The plasma pre-treatment may preferably comprise subjecting the surface segment of the substrate to an oxidizing gas in the absence of monomer.

30 The oxidizing gas in the pre-treatment may preferably comprise one or more oxidizing components selected from the group consisting of O₂, N₂O and mixtures thereof. In one embodiment the oxidizing gas comprises one or more oxidizing components in combination with one or more inert gasses selected from the group consisting of argon, helium, neon and krypton.

35

In one embodiment where the substrate surface segment is of inorganic material, the pre-treatment comprises cleaning and or activation of the surface segment in a reduction gas plasma (e.g. using H₂ gas), optionally followed by a pre-treatment comprising subjecting the surface segment of
5 the substrate to an oxidizing gas.

In one embodiment where the substrate surface segment is of metal or polymer, the pre-treatment comprises cleaning and or activation of the surface segment in a reduction gas plasma (e.g. using H₂ gas), optionally
10 followed by applying a primer layer.

The surface segment of the substrate may be all of the substrate or one or more parts of the substrate surface.

15 The surface segment may additionally be subjected to a post-treatment i.e. a treatment performed onto the applied primer layer but prior to applying the elastomer. The post-treatment may preferably be a plasma treatment e.g. a plasma treatment with an oxidizing component in a plasma in the absence of monomer. The oxidizing component may preferably be oxygen, N₂O or CO₂.

20 The post-treatment may e.g. be performed for up to 15 minutes, preferably between 0.5 and 5 minutes, such as between 1 and 3 minutes.

25 The method comprises overmolding an elastomer onto at least a part of the treated surface segment of the substrate. The overmolding may preferably comprise applying the elastomer in non-cured or partly-cured condition onto the substrate and curing the elastomer.

30 The overmolding may in one embodiment comprise applying the substrate and the elastomer in a mould simultaneously or one after the other, followed by curing the elastomer preferably under pressure. In embodiments where the elastomer is cured under pressure the elastomer may be applied to the substrate in partly-cured condition. The obtained bonding between substrate and elastomer has shown to be very strong even when only the final curing is
35 performed when the elastomer is in contact with the substrate.

In one embodiment the overmolding comprises applying the elastomer onto at least a part of the substrate surface, by spraying, brushing, dipping, printing, laminating or rolling, followed by curing the elastomer.

5

In one embodiment the overmolding comprises shaping and partly curing the elastomer, and applying the substrate in contact with the elastomer and allowing the elastomer to proceed curing. In this embodiment is preferred that the substrate and the partly cured elastomer is pressed together. The

10 pressure need not be maintained during the final curing process but it is desired that the pressure is maintained at least for 10 seconds, such as at least 20 seconds, such as at least 1 minutes. The pressure may be applied manually or by machine. In one embodiment the method comprises applying a pressure to hold together the substrate and the partly cures elastomer, the
15 pressure preferably being at least 1 N per m² substrate segment, such as at least 5 N per m² substrate segment, such as at least 10 N per m² substrate segment.

In one embodiment the overmolding comprises

20 - melting and applying the elastomer to the substrate by one or more of the methods pressing, extrusion, injection moulding, thermoforming, thermo moulding, calendaring, rotation moulding, compression moulding and transfer moulding and allowing the elastomer to cure.

25 The elastomer may be cured using any method e.g. using conventional heat and/or electromagnetic waves such as IR, micro wave, UV and combinations thereof.

The elastomer should prior to application onto the substrate be capable of
30 curing.

Preferably the elastomer is a rubber. Preferred rubbers includes rubbers selected from silicone rubber, fluoro elastomer rubber (e.g. based on hexafluoropropylene vinylidene fluoride), and acrylonitrile-butadiene rubber
35 (NBR), polyacrylate rubber, hydrated NBR, styrene-butadiene-rubber (SBR),

natural rubber (NR), ethylene-propylene-diene-rubber (EPDM), Isoprene-rubber (IR), polyester-urethane and polyether-urethane.

5 In a preferred embodiment the rubber is silicone rubber, such as silicone rubber selected from liquid silicone elastomers (LSR), RTV-1 silicone rubbers, RTV-2 silicone elastomers and HTV silicone elastomers, the silicone rubber preferably being selected from functionalized silicone rubbers such as fluoro silicone rubbers and self adhesive silicone rubbers.

10 In one embodiment the elastomer is silicone rubber comprising one or more of the silicone components selected from the group consisting of dialkylsilicone elastomers wherein alkyl means hydrocarbon side groups of 1-12 carbon atoms such as methyl, ethyl, hexyl, and octyl; vinyl silicone elastomers; phenyl silicone elastomers; nitrile silicone elastomers; 15 fluorosilicone elastomers, room temperature vulcanising (RTV) silicone elastomers; liquid silicone elastomers (LSR); borosilicone elastomers, and dimethyl silicone elastomers.

20 The silicone rubber may preferably be cross-linked using a method selected from the group of condensation reaction, addition reaction, peroxide assisted reaction, platinum catalyzed, rhodium catalyzed reaction and mixtures thereof.

25 In a preferred embodiment the method of the invention comprises

- providing a non-elastomer substrate,
- treating at least a surface section of said substrate in a plasma comprising pre-treating using an oxidating gas and depositing at least one primer layer in the form of a Si-oxide network optionally 30 comprising other atoms than Si in the oxide network, the total thickness of the at least one primer layer being up to 200 nm; and
- overmolding a rubber onto said primer treated substrate

35 The invention also relates to an item obtainable using the method as described above. The invention further relates to an overmolded item comprising a

substrate and an elastomer bonded to each other and with an interface layer having a composition which is not merely a mixture of the composition of the substrate and the elastomer, wherein said interface layer has a thickness of 200 nm or less measured using SEM (Scanning electron microscope).

5

The substrate and the elastomer may be as described above.

The primer layer(s) may be obtainable by the method and using the materials as described above.

10

In one embodiment the interface layer has a thickness of 150 nm or less, such as a thickness 100 nm or less, such as a thickness of 50 nm or less.

In one embodiment the interface layer has a glasslike structure, the interface layer preferably comprises an oxide network of Si and optionally other atom(s).

15

In one embodiment the bonding between the substrate and the elastomer is stronger than the intrinsic strength of at least one of the substrate and the elastomer.

20

EXAMPLES

The invention will be explained more fully below in connection with the below examples.

25

Further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

30

35 Example 1

Glass / silicon like coating on Polyamide (PA) substrate

The plasma treatment was made in an equipment with a reaction chamber
5 volume of around 290 L, and supplied with a 50 Hz power supplier.

4 samples (20 cm x 5 cm x 0.4 cm) of PA were applied in the reaction
chamber. The reaction chamber was evacuated and the samples were
subjected to a pre-treatment and a treatment (application of primer)
10 according to the following scheme.

Plasma treatment parameters:

Monomer: (Tetramethoxysilane)

Step	Ar ml/min	Monomer ml/min	Energy W	Time min	Pressure Pa
pre- treatment	40	0	240	0.3	4.7
Treatment	40	40	240	2	6.3 - 6.8

15

The obtained primer layer is not pure inorganic, but contains some organic
parts.

The treated substrates as well as 4 corresponding samples which were not
20 treated by plasma (free of primer) were overmolded with an elastomer.

The elastomer was applied manually onto the substrate by an applicator to
obtain a thickness of about 1mm. Then the elastomer was covered by a
PTFE and slightly pressed (about 200 g) and applied in a heating chamber
25 where the elastomer was cured 5 min at 150 °C.

Elastomer: LSR from Nusil (MED-5850)

Test results:

Test name	Adhesion	comments
Standard sample (no plasma treatment)	Very poor	The silicone can be separated very easy from the PA.
Plasma treated	Very good	There is a good adhesion between PA and silicone. In an attempt to separate the PA from the Silicone, the PA is damaged.

5 Example 2

Glass coating on Polycarbonate (PC)

10 The plasma treatment was made in equipment with a reaction chamber volume around 30 L, and a power supplier (Tantec) of 1 kW (30k Hz).

4 samples (20 cm x 2 cm x 0.4 cm) of PC were applied in the reaction chamber. The reaction chamber was evacuated and the samples were subjected to a pre-treatment, 6 treatment steps (application of a graduated primer layer) and a post-treatment according to the following scheme.

15

Plasma treatment parameters:

Monomer: Tetramethoxysilane (TMOS) from ABCR

20

25

Step	O ₂ ml/min	Ar ml/min	Monomer ml/min	Energy W	Time min	Pressure Pa
pre-treatment	0	15	0	80	0.3	7
Treatment 1	0	15	12	80	1	9.5
2	10	10	12	80	1	11.6
3	15	5	12	100	1	12.5
4	20	1	12	120	1	12.8
5	25	1	12	180	1	14.1
6	25	1	12	250	1	13.8
Post treatment	25	1	0	200	1	10.0

The plasma treatment was initiated by applying a soft organic primer layer (silicon like coating) and by changing the energy and increasing the oxygen feeding, the primer layer becomes gradually more and more inorganic (glass coating). At the end the post treating will remove the organic part and make the surface pure inorganic glass coating.

The treated substrates as well as 4 corresponding samples which were not treated by plasma (free of primer) were overmolded with an elastomer.

10

2 of the plasma treated samples and two of the non-treated samples were overmolded with an LSR silicone and the 2 other of the plasma treated samples and two of the non-treated samples were overmolded with RTV silicone.

15

The elastomers were applied manually onto the respective substrates, LSR was covered with PTFE foil, slightly pressed (200g) and applied in a heating chamber where the elastomer was cured 5 min at 150°C. RTV was applied in a thin layer on the substrate and cured 24 h at room temperature.

20

Elastomers: 2K LSR from Wacker, and RTV silicone Dow corning 738 and 3140).

Test results:

5

Test name	Elastomer	Adhesion	comments
Standard sample (no plasma treatment)	2K LSR	Very poor	The silicone can be separated very easy from the PC.
Standard sample (no plasma treatment)	RTV	Very poor	The silicone can be separated very easy from the PC.
Plasma treated	2K LSR	Very good	Excellent adhesion between PC and silicone.
Plasma treated	RTV	Very good	Excellent adhesion between PC and silicone.

Example 3

Organic coating on Polycarbonate (PC), and Polyethylene terephthalate (PET)

10

The plasma treatment was made in an equipment with a reaction chamber volume around 12 L, and power supplier (3 fazes) 50 Hz.

15 2 samples (discs, 12 cm in diameter) of PC and 2 samples (discs, ø 12 cm in diameter) of PET were applied in the reaction chamber. The reaction chamber was evacuated and the samples were subjected to a pre-treatment and a treatment (application of a primer layer) according to the following scheme.

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Plasma treatment parameters:

Monomer: Acrylnitrile (AN) from Aldrich

Step	Ar ml/min	Monomer ml/min	Energy W	Time min	Pressure Pa
pre-treatment	7	7	12	0.5	6.7
Treatment	7	7	12	6	7.6

The obtained primer layer is pure organic.

5

The treated substrates as well as 4 corresponding samples which were not treated by plasma (free of primer) were overmolded with an elastomer.

10 The elastomer was applied manually onto the substrate and pressed together with 1000 N at 130 °C for 2 min.

Elastomer: TPU like silicone from Wacker.

Test results:

Test name	Adhesion	comments
Standard sample (no plasma treatment)	Very poor	The silicone can be separated very easily from the PC.
Plasma treated	Very good	Good adhesion between PC and silicone.

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Some preferred embodiments have been shown in the foregoing, but it should be stressed that the invention is not limited to these, but may be embodied in other ways within the subject-matter defined in the following claims.

20

CLAIMS

1. A method of producing an item comprising
 - providing a substrate,
 - 5 • treating at least a surface section of said substrate by applying at least one primer layer, the total thickness of the at least one primer layer being up to 200 nm; and
 - overmolding an elastomer onto and/or into said primer treated substrate.
- 10
2. A method of producing an item as claimed in claim 1, wherein the substrate being a solid substrate, preferably selected from the group consisting of polymer, such as polyethylene (PE) polypropylene (PP),
15 polycarbonate (PC), polyamide (PA) , poly(phenylene sulphide) (PPS), polymethylmethacrylate (PMMA), polystyrene (PS), polyethylene terephthalate (PET), and fluoropolymers; carbon or aramide (preferably in the form of fibers or particles); glass; metal, such as iron, steel (stainless, duplex and other), aluminium, magnesium; and/or ceramic material, such as
20 oxide based ceramic materials, (alumina, zirconia), non-oxide based ceramic materials, (carbides, borides, nitrides, silicides), and/or composites thereof.
3. A method of producing an item as claimed in any one of claims 1 and 2, wherein the substrate is a film, having an essentially even thickness,
25 preferably of 2 mm or less, such as 1 mm or less, such as 0.5 mm or less, such as 0.1 mm or less, such as 0.05 mm or less.
4. A method of producing an item as claimed in any one of the preceding claims wherein the substrate has at least one thickness larger than 0.5 mm,
30 the item preferably has a non-plane surface section, such as a curved and/or edged surface section.
5. A method of producing an item as claimed in any one of the preceding claims wherein the substrate is essentially nonflexible, and preferably have a

an inherent stiffness of at least 100, such as between 10^3 and 10^{10} N/m, such as between 10^4 and 10^6 N/m.

6. A method of producing an item as claimed in any one of the preceding
5 claims wherein the primer layer(s) being applied using plasma deposition of at least one monomer, the plasma preferably being a low (lower than atmosphere) pressure AC (alternating current) or DC (direct current) plasma, wherein the pressure in the plasma during deposition treatment preferably being is 50 Pa or below, below 35 Pa, such as between 1 and 30 Pa.

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7. A method of producing an item as claimed in claim 6, wherein the plasma being a low power plasma, preferably the applied power being 100 W/l plasma reactor or less, such as 50 W/l plasma reactor or less, such as 30 W/l plasma reactor or less, such as 20 W/l plasma reactor or less, such
15 as 10 W/l plasma reactor or even less, such as 5 W/l plasma reactor or less, such as 3 W/l or less, such as 1 W/l or even less.

8. A method of producing an item as claimed in any one of the claims 6 and 7, wherein the plasma being a one phase plasma (one electrode or
20 electrode group having same voltage and one grounded electrode/electrode group) operating at a frequency of 50 Hz to 15 MHz, such as to 13.6 MHz.

9. A method of producing an item as claimed in any one of the claims 6-8, wherein the plasma deposition comprising applying the substrate in a plasma
25 reactor, reducing the pressure in the plasma reactor, feeding the at least one monomer to the plasma reactor preferably together with a support gas selected from the group consisting of inert gases, oxidizing gasses or reducing gasses, the support gas preferably being selected from the group consisting of N_2O , Ar, O_2 , H_2 , N_2 and mixtures thereof.

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10. A method of producing an item as claimed in any one of the claims 6-9, wherein the total thickness of the at least one primer layer being in the interval between 1 and 150 nm, such as between 5 and 100 nm, such as between 10 and 70 nm.

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11. A method of producing an item as claimed in any one of the claims 6-10 wherein the at least one monomer being selected such that the deposited layer being essentially inorganic.
- 5 12. A method of producing an item as claimed in any one of the claims 6-10 wherein the at least one monomer being selected such that the deposited layer being organic.
- 10 13. A method of producing an item as claimed in any one of the claims 6-12, wherein the at least one monomer comprises a Si containing monomer, preferably selected from the group consisting of silanes and/or organosilicon compositions such as hexamethyldisiloxane, methoxytrimethylsilane, tetramethoxysilane, hexamethylcyclotrisiloxane, methyltriethoxysilane, and phenyltriethoxysilane.
- 15 14. A method of producing an item as claimed in any one of the claims 6-13, wherein the one or more monomers comprising at least one monomer selected from silane, hexamethyldisiloxane, tetramethoxyxilane and tetraethoxysilane, the monomer being fed into the reaction chamber together
20 with an oxidating composition such as O₂.
- 25 15. A method of producing an item as claimed in any one of the claims 6-14, wherein the plasma deposition comprising, feeding the at least one monomer to the plasma reactor together with a support gas comprising an inert gas component, such as Ar and/or an oxidizing gas component, such as O₂ or N₂O the monomer(s) being selected to form a glass layer in the form of an oxide network including Si atoms.
- 30 16. A method of producing an item as claimed in any one of the claims 6-15, wherein the one or more monomers comprising at least one monomer selected from hexamethylsiloxane, tetramethoxysilane and tetraethoxysilane.
17. A method of producing an item as claimed in any one of the claims 6-16, wherein O₂ being fed to the chamber in a molar ratio monomer:O₂ of

from 20:1 to 1:20, such as from 10:1 to 1:10, such as from 5:1 to 1:5, such as from 2:1 to 1:2, such as about 1:1.

18. A method of producing an item as claimed in any one of the claims 6-
5 17, wherein Ar being fed to the chamber in a molar ratio monomer:Ar of from 10:1 to 1:10, such as from 5:1 to 1:5, such as from 3:1 to 1:3, such as from 2:1 to 1:2, such as about 1:1.

19. A method of producing an item as claimed in any one of the claims 6-
10 18, wherein the method comprising applying a graduated primer layer, the method comprising feeding at least two monomers in amounts which are varied relative to each other during the deposition treatment.

20. A method of producing an item as claimed in any one of the claims 6-
15 19, wherein the method comprising applying one single primer layer.

21. A method of producing an item as claimed in any one of the claims 6-19, wherein the method comprising applying two or more primer layers.

20 22. A method of producing an item as claimed in claim 21, wherein the two or more primer layers comprising at least one glass layer in the form of an oxide network including Si atoms, preferably all primer layers are in the form of glass layers comprising an oxide network including Si atoms.

25 23. A method of producing an item as claimed in any one of the claims 21-22, wherein the method comprising applying alternating Si-oxide network and Si-C-oxide network layers, wherein the layers independently of each other optionally comprise up to 50 % by atom mol of the respective layer composition of carbon.

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24. A method of producing an item as claimed in any one of the claims 21-23, wherein the method comprising

- applying a first primer layer comprising feeding one or more of the monomers selected from the group of siloxanes;

- applying a second primer layer onto the first primer layer comprising feeding one or more of the monomers selected from the group of alkanes, alkenes, alkynes, alcohols, amines, ammonia compounds with vinyl and/or allyl groups, compounds with ester and/or acid groups and compounds with fluoro groups.

25. A method of producing an item as claimed in any one of the claims 21-24, wherein the two or more primer layers being applied immediately after each other in same plasma treating process.

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26. A method of producing an item as claimed in any one of the preceding claims wherein the method comprising pre-treating the surface segment of the substrate prior to applying the primer layer.

15 27. A method of producing an item as claimed in claim 26, where the pre-treatment comprises subjecting the surface segment of the substrate to an oxidizing gas, the oxidizing gas in the pre-treatment preferably comprises one or more oxidizing components selected from the group consisting of O₂, N₂O and mixtures thereof, the oxidizing gas preferably comprises one or
20 more oxidizing components in combination with one or more inert gasses selected from the group consisting of argon helium neon and krypton.

28. A method of producing an item as claimed in any one of claims 26 and 27, where the substrate surface segment is of inorganic material, the pre-treatment comprises cleaning and or activation of the surface segment in a
25 reduction gas plasma (e.g. using H₂ gas), optionally followed by a pre-treatment comprising subjecting the surface segment of the substrate to an oxidizing gas.

30 29. A method of producing an item as claimed in any one of claims 26 and 27, where the substrate surface segment is of metal or polymer, the pre-treatment comprises cleaning and or activation of the surface segment in a reduction gas plasma (e.g. using H₂ gas), optionally followed by applying a primer layer.

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30. A method of producing an item as claimed in any one of the preceding claims wherein the method comprises overmolding an elastomer onto at least a part of said treated surface segment of said substrate, the overmolding comprising applying the elastomer in non-cured or partly-cured
5 condition onto the substrate and curing the elastomer.

31. A method of producing an item as claimed in claim 30 wherein the overmolding comprises applying the substrate and the elastomer in a mould simultaneously or one after the other, followed by curing the elastomer
10 preferably under pressure and / or heat.

32. A method of producing an item as claimed in claim 30 wherein the overmolding comprises applying the elastomer onto at least a part of the substrate surface, by spraying, brushing, dipping, printing, laminating or
15 rolling, followed by curing the elastomer.

33. A method of producing an item as claimed in claim 30 wherein the overmolding comprises shaping and partly curing the elastomer, and applying the substrate in contact with the elastomer and allowing the
20 elastomer to proceed curing.

34. A method of producing an item as claimed in claim 30 wherein the overmolding comprises
- melting and applying the elastomer to the substrate by one or more of the
25 methods pressing, extrusion, injection moulding, thermoforming, thermo moulding, calendaring, rotation moulding, compression moulding and transfer moulding and allowing the elastomer to cure.

35. A method of producing an item as claimed in any one of the preceding
30 claims wherein the elastomer is cured using conventional heat and/or electromagnetic waves such as IR, micro wave, UV and combinations thereof.

36. A method of producing an item as claimed in any one of the preceding
35 claims wherein the elastomer is a rubber, preferably selected from silicone

rubber, fluoro elastomer rubber (e.g. based on hexafluoropropylene vinylidene fluoride), and acrylonitrile-butadiene rubber (NBR), polyacrylate rubber, hydrated NBR, styrene-butadiene-rubber (SBR), natural rubber (NR), ethylene-propylene-diene-rubber (EPDM), Isoprene-rubber (IR), polyester-urethane and polyether-urethane.

37. A method of producing an item as claimed in claim 36 wherein the elastomer is silicone rubber selected from liquid silicone elastomers (LSR), RTV-1 silicone rubbers, RTV-2 silicone elastomers and HTV silicone elastomers, the silicone rubber preferably being selected from functionalized silicone rubbers such as fluoro silicone rubbers and self adhesive silicone rubbers.

38. A method of producing an item as claimed in claim 36 wherein the silicone rubber comprises one or more of the silicone components selected from the group consisting of dialkylsilicone elastomers wherein alkyl means hydrocarbon side groups of 1-12 carbon atoms such as methyl, ethyl, hexyl, and octyl; vinyl silicone elastomers; phenyl silicone elastomers; nitrile silicone elastomers; fluorosilicone elastomers, room temperature vulcanising (RTV) silicone elastomers; liquid silicone elastomers (LSR); borosilicone elastomers, and dimethyl silicone elastomers.

39. A method of producing an item as claimed in any one of claims 36-38 wherein said silicone rubber is cross-linked, preferably by a method selected from the group of condensation reaction, addition reaction, peroxide assisted reaction, platinum catalyzed, rhodium catalyzed reaction and mixtures thereof.

40. A method of producing an item as claimed in any one of the preceding claims wherein the method comprising

- providing a non-elastomer substrate,
- treating at least a surface section of said substrate in a plasma comprising pre-treating using an oxidizing gas and depositing at least one primer layer in the form of a Si-oxide network optionally

comprising other atoms the Si in the oxide network, the total thickness of the at least one primer layer being up to 200 nm; and

- overmolding a rubber onto said primer treated substrate.

5 41. An item obtainable using the method as claimed in any one of the preceding claims.

42. An overmolded item comprising a substrate and an elastomer bonded to each other and with an interface layer having a composition which is not
10 merely a mixture of the composition of the substrate and the elastomer, wherein said interface layer has a thickness of 200 nm or less measured e.g. using SEM (Scanning electron microscope).

43. An overmolded item as claimed in claim 42, wherein said interface layer
15 has a thickness of 150 nm or less, such as a thickness 100 nm or less, such as a thickness of 50 nm or less.

44. An overmolded item as claimed in any one of claims 42 and 43, wherein
20 said interface layer has a glasslike structure, the interface layer preferably comprises an oxide network of Si and optionally other atom(s).

45. An overmolded item as claimed in any one of claims 42- 44, wherein the
25 bonding between the substrate and the elastomer is stronger than the intrinsic strength of at least one of the substrate and the elastomer.

INTERNATIONAL SEARCH REPORT

International application No

PCT/DK2008/050246

A. CLASSIFICATION OF SUBJECT MATTER

INV. B32B7/02 C08J7/00 C09D4/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B32B C08J C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 378 535 A (MONCUR MARLOWE V [US] ET AL) 3 January 1995 (1995-01-03) column 3, lines 56-59 claim 1	1,42
X	US 4 374 694 A (BLENNER DONALD R ET AL) 22 February 1983 (1983-02-22) column 4, lines 56-59 claims 1-8	1,42
X	EP 0 110 258 A (SHINETSU CHEMICAL CO [JP]) 13 June 1984 (1984-06-13) claims 1-5	1,42



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

8 document member of the same patent family

Date of the actual completion of the international search

4 March 2009

Date of mailing of the international search report

12/03/2009

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/DK2008/050246

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