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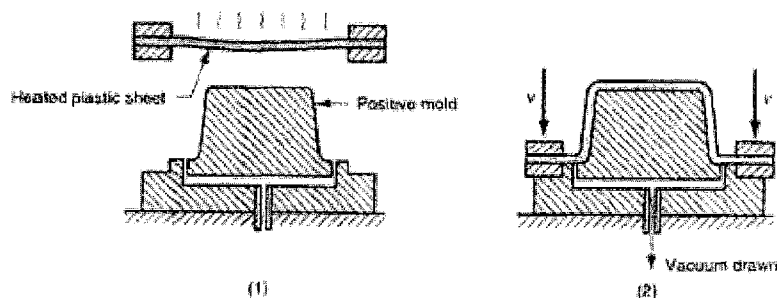
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(54) Title: METHOD OF PRODUCING SHAPED ARTICLES FROM A UV-CURABLE SILICONE RUBBER COMPOSITION

Fig. 1



(57) Abstract: Method of producing a shaped article from a UV-curable silicone rubber composition by irradiating said UV-curable silicone rubber composition with UV-light, comprising the steps of (i) filling a UV-curable silicone rubber composition into a thermoformed UV-transparent mould which is made from a thermoplastic UV-transparent polymer, and (ii) curing said UV-curable silicone rubber composition within said thermoformed UV-transparent mould by irradiation with UV-light; said shaped articles being in the form of an electrical insulator for indoor and outdoor use; and electrical articles comprising an electrical insulation made by the method according to the present invention.

Method of Producing Shaped Articles from a UV-curable Silicone Rubber Composition

Field

5 The present writing relates to a method of producing shaped articles from a ultra-violet light (UV) curable silicone rubber composition by using a thermoformed UV-transparent mould and curing said UV-curable silicone rubber composition within the thermoformed UV-transparent mould with a UV-light source. Said
10 shaped articles preferably are electrical insulators for indoor and outdoor use, preferably high voltage electrical insulators. Said thermoformed UV-transparent mould is made from a thermoplastic UV-transparent polymer, and preferably is made from a thermoplastic UV-transparent and UV-stable polymer. Said
15 UV-light source preferably is a UV-LED light source.

State of the Art

In the electrotechnical industry silicone compositions are used as electrical insulations both for indoor and outdoor applications, for example as hollow core insulators, cable accessories such as cable terminations, medium voltage and high voltage surge arresters, or vacuum interrupters. For these applications high temperature vulcanizing silicone rubber (HTV-SR) compositions and room temperature vulcanizing silicone rubber (RTV-SR) compositions, including liquid silicone rubber (LSR) compositions, are used. In the case of RTV-SR and LSR compositions, the curable silicone rubber composition is generally composed of two components, namely a first component comprising at least one polysiloxane having alkenyl groups, such as vinyl groups, incorporated in the molecule, and a second component comprising at least one polysiloxane having $\equiv\text{SiH}$ -groups incorporated in the molecule. These two components are mixed, filled into a mould and cured in the presence of a catalyst, e.g. a UV sensitive cross-linking catalyst. Such UV-curable silicone rubber compositions being curable in the presence of UV-radiation are known in the art and are described for example in WO 2006/010763 A1

and WO 2009/027133 A2, the contents of which are incorporated herein by reference.

5 UV-curable silicone rubber compositions cure very fast under the influence of UV-light even for large thicknesses of several centimeters. This is of importance as the curing time plays a significant role in the production and cycle time of such products.

10 Quartz moulds have been developed to manufacture insulators made from UV-curable silicone rubber compositions as described for example in WO2007065766 A1. Quartz has the advantage of being transparent for UV-radiation, i.e. is UV-transparent, as well as being stable to UV-radiation, i.e. is UV-stable. However, quartz
15 has the disadvantage of being brittle. Quartz moulds further are difficult to produce on an industrial scale and their production is comparatively cost intensive when compared to the production of steel moulds. Therefore, there is a need for simple and comparatively cheap moulds for the use in the production of shaped
20 articles such as electrical insulators which are made from UV-curable silicone rubber compositions.

Summary

It has now been found that it is possible to produce UV-cured
25 shaped articles from UV-curable silicone rubber compositions by using moulds which are made substantially entirely from thermoplastic UV-transparent polymeric materials. These moulds or at least parts or portions thereof are manufactured of sheet material, also known as semi-finished, planar sheet products
30 having a constant thickness, in particular standard sheet material that is commercially available and inexpensive. That sheet material is being brought in such a shape, e.g. by thermoforming, such that its interior contour is the negative or the positive of the form of the article to be shaped with the
35 moulds. Depending on the complexity and the cross-section of the article to be shaped by the molds, a single mold, two halve-

moulds that are matching one another or multi-part moulds comprising several mold portions may be required.

Preferred are moulds that are substantially made from thermo-
5 plastic UV-transparent and UV-stable polymeric sheet materials.
The wall thickness of such moulds can vary between about 1 mm to
50 mm, depending on the size of the article to be shaped and the
amount of the UV curable composition, e.g. a UV curable silicone
10 rubber composition, that needs to be supported and prevented
from deforming the moulds or mould portions for the article to
be shaped by the moulds. Expressed differently, moulds having a
wall thickness of more than 1 mm can carry heavier weight
15 fillings of the UV curable composition than moulds having a wall
thickness of 1 mm only.

15 Using thermoformed thermoplastic UV-transparent moulds according
to the present invention allows using moulds which are easy and
comparatively cheap to produce with conventional methods, espe-
cially with thermoforming techniques, also on an industrial
20 scale. This renders the production of UV-cured shaped articles
made from UV-curable silicone rubber compositions considerably
cheaper and further very flexible with respect to technical
feasibility. For example, when a mould is damaged due to
handling or ageing, it can easily be replaced. Moreover, the
25 method according to the present invention allows the manufacture
of large moulds which are not possible to manufacture by other
means, such as by machining or injection moulding techniques.
This is of particular interest for the manufacture of large
articles, such as electrical insulators like hollow core
30 insulators.

A further advantage resides in that also large moulds of several
meters length can be manufactured from thermoformed sheet
material since standard PMMA sheets of 2 by 3 meters, for
35 example, are available and are thermoformable on suitable
forming machinery.

A further advantage of the moulds that are made of solid sheet material resides in a comparatively low mass or weight compared to moulds that are made of a cylindric, for example prismatic transparent blocks that are machined thereafter for creating the negative form of the article to be shaped. Nonetheless are the inventive molds rigid enough to be re-used in a subsequent moulding process of a new shaped article after demoulding a previous shaped article moulded therein.

A further advantage is the use of the thermoformed thermoplastic mould of the present invention in the manufacture of UV-cured shaped articles made from UV-curable silicone rubber compositions in combination with UV-LED lamps. Due to the low heat emission of UV-LED lamps, the lamps can be placed very close to the wall of the thermoformed mould without damaging the plastic mould. This enhances the curing of the UV-curable silicone rubber composition.

The mould concept of the present invention may be combined with UV-reflecting materials like aluminum foils or polished aluminum parts in order to optimize the UV-exposure of the part to be moulded.

Drawings

The present technology will be better understood but not limited by the attached drawings where:

Figure 1 pictorially shows a first step and a second step of attending to a mould;

Figure 2 illustrates a thermoplastic mould within a frame and around an insert.

Description

The present invention is defined in the claims. Specifically, the present invention refers to a method of producing shaped articles from a UV-curable silicone rubber composition by irradiating said UV-curable silicone rubber composition with UV-light, characterized by the steps of (i) filling a UV-curable

silicone rubber composition into a thermoformed UV-transparent mould which is made from a thermoplastic UV-transparent polymer, which preferably is also a UV stable polymer, and (ii) curing said UV-curable silicone rubber composition within said thermo-
5 formed UV-transparent mould by irradiation with UV-light.

Said shaped articles preferably are electrical insulators for indoor and outdoor use, preferably high voltage electrical insulators. For providing an electrical device, for example a
10 hollow core, with the electrical insulation composition, said electrical device is placed and fixed in the thermoformed UV-transparent mould, so that there remains a defined free space between the outer surface of the electrical device and the inner mould walls. The UV-curable silicone rubber composition is then
15 filled into the thermoformed UV-transparent mould so that the free space between the outer surface of the electrical device and the inner mould walls is filled with the UV-curable silicone rubber composition, which subsequently is cured by irradiation with UV-light.

20

The present invention refers to a thermoformed UV-transparent mould which is preferably entirely made from a thermoplastic UV-transparent polymer and preferably entirely made from a thermoplastic UV-transparent and UV-stable polymer.

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The present invention further refers to shaped articles, preferably in the form of an electrical insulator for indoor and outdoor use, preferably as a high voltage electrical insulator, made from a UV-curable silicone rubber composition by irradiating said UV-curable silicone rubber composition with UV-light,
30 characterized in that said UV-curable silicone rubber composition has been filled into a thermoformed UV-transparent mould substantially made from a thermoplastic UV-transparent polymer, and that curing of said UV-curable silicone rubber composition
35 within the thermoformed UV-transparent mould was performed by irradiation with UV-light.

The present invention further refers to electrical articles comprising an electrical insulation made from a UV-curable silicone rubber composition by irradiating said UV-curable silicone rubber composition with UV-light, said electrical insulator
5 having been produced in a thermoformed UV-transparent mould made from a thermoplastic UV-transparent polymer, as defined herein according to the present invention.

There are many thermoplastic polymers that are UV-transparent
10 and UV-stable. Such commercially available polymers are known in the art and can be used for the production of moulds within the scope of the present invention. Thermoplastic polymers that are UV-transparent and UV-stable, resp. are UV-transparent engineering plastics, are for example polymethylmethacrylate (PMMA);
15 polyvinylchloride (PVC); cyclo-olefine-polymers (COP) as commercially available under the trade names ZEONE®, or ZEONOR®; polymethylacryl-methylimide-polymers (PMMI); polycarbonate (PC); polyethylene-terephthalate (PET); styrene-acrylonitrile polymers (SAN); polysulfone polymers (PSU); polymethacrylimide polymers
20 (PMI); polypropylene (PP); polystyrene (PS). Preferred are polymethylmethacrylate (PMMA); polyvinylchloride (PVC); cyclo-olefine-polymers (COP); polymethylacryl-methylimide-polymers (PMMI); polycarbonate (PC); and polyethylene-terephthalate (PET). Most preferred are polymethylmethacrylate (PMMA) and
25 polyvinylchloride (PVC).

A UV-transparent thermoplastic polymer within the scope of the present invention is a polymer with a UV-transparency of at least 30%, preferably of at least 60%, preferably of at least
30 80%, and preferably of at least 90%. For example with 60% UV-transparency in a wavelength range of the UV spectrum of the material of about 360 nm to 380 nm. If other transparencies are selected the wavelength need to be adjusted accordingly.

35 In this sense the wall thickness of the mould, i.e. the UV transparent mould wall, can vary between about 1 mm and 50 mm, giving

the possibility to manufacture either flexible or rigid transparent moulds.

5 In an embodiment the wall thickness of the mould is within the range of about 1.0 mm to about 50 mm, preferably higher than 1 mm, preferably within the range of about 2.0 mm to about 30 mm, preferably within the range of about 2.0 mm to about 15 mm, preferably within the range of about 2.0 mm to about 10 mm. A thickness that is within the indicated range is typically enough
10 to provide a mould that is durable for multiple mould cycles and to carry heavier weights. The wall thickness has to be selected such that the sheet material can be heated up for conducting the thermoforming process in order to create the negative or positive form of the article to be shaped.

15 The moulds can be produced for example from sheets with thermoplastic methods as single thick wall parts which are then put together to form a closed tool. Where required, the molds are assembled of several mould parts that are welded together. Such
20 molds may contain more than one cavity that can be closed using e.g. snap lock solutions, to form a closed tool. For example vacuum forming techniques can be used for forming conical shaped mould tool parts, such as conical outer mould parts for forming stress relief cones.

25 Test results have shown that commercially available UV-curable silicone rubber compositions when cured with UV-light in moulds made from UV-transparent and UV-stable thermoplastic polymers, resp. in moulds made from UV-transparent engineering plastics,
30 as defined herein above, cure within a curing time of about 10 seconds to 60 seconds, and generally within a curing time of about 30 seconds.

The moulds can be produced for example as single thick wall
35 parts which are then put together to form a closed tool. It is also possible to manufacture molds that contain more than one

cavity, that can be closed using e.g. snap lock solutions, to form a closed tool.

For example vacuum forming techniques can be used for forming
5 conical shaped mould tool parts, such as conical outer mould parts for forming stress relief cones. For such moulds for example PVC sheets of 1 mm thickness as blanks can be used.

Figure 1 illustrates the mould manufacture with UV-transparent
10 plates that are heated up and formed on a positive mould. The two mould halves are then mounted together for example using a frame. Figure 2 illustrates a possible moulding concept.

The core of the mould, made from a UV-transparent engineering
15 plastics, for example made from a PMMA tube, may be designed to hold an aluminium foil in order to scatter the UV-light to shadowed parts of the UV-curable SR-composition within the mould.

20 Mixing and metering equipments for mixing the components of the UV-curable liquid silicone rubber composition (UV-LSR) and for filling the moulds with the UV-LSR is known and commercially available.

25 As a light source for irradiation with UV-light any light source can be used. Such UV-light sources are commercially available. The wavelength generally is within the range of 180 nm to 700 nm, preferably within the range of 190 nm to 500 nm, preferably within the range of 300 nm to 400 nm, and preferably at
30 about 360 nm to 400 nm.

UV-light sources to produce UV-light, which can be used within the scope of the present invention, are for example xenon lamps, mercury lamps and mercury lamps doped with iron or gallium,
35 black-light lamps, excimer lasers and UV-LED lamps.

The UV-light source may be provided for example by an arcing UV-lamp, or by a microwave powered UV-lamp or by an LED UV-lamp.

The major advantage of LED UV-lamp over the two other types of UV-lamps is the fact that an LED UV-lamp irradiates within a specific wavelength area. In this way, a significantly lower amount of heat is generated during UV-irradiation. Therefore,
5 LED UV-lamps are preferred to work with transparent organic moulds.

Preferred is a light source based on the UV-LED technique, particularly in the form of the Semiconductor Light Matrix
10 (SLM), as closed packed LED's. Such a light source is simple to install, is safe to use and energy efficient, and has a long service life with practically no maintenance costs. UV-LED sources further have a high UV-light intensity and give good curing results, for example when comparing cure depth versus
15 distance of the UV-light source and irradiation time, for UV-curing UV-LSR compositions. UV-LED sources generally give better results than conventional halogen UV-sources, as the the UV-intensity of UV-LED sources is generally higher than the UV-intensity of conventional halogen UV-sources. An example for
20 a commercially available UV-lamp is the Phoseon water cooled UV-LED RX StarFire Max, with wavelength of 365 nm and 395 nm with a stated output of 2 W/cm² or 4 W/cm².

The UV-curable silicone rubber composition may contain sensi-
25 zers and/or photoinitiators such as compounds derived from anthracene, xanthone, anthrachinone. Such compounds and their use as sensitizers and/or photoinitiators are known in the art and are commercially available.

30 The irradiation source preferably has power consumption within the range of 2 kW to 20 kW and may be arranged around the mould at a distance of 1 cm to 100 cm, preferably at a distance of 1 cm to 10 cm, whereby the mould may be rotated so as to uniformly distribute the irradiation energy.

35

The UV-light-irradiation intensity applied for UV-curing LSR is preferably within the range of 1 W/cm² to 4 W/cm², preferably

within the range of 2 W/cm² to 4 W/cm², at a wave length as defined herein before.

5 A common UV-source used today for UV-curing different curable materials are mercury lamps and mercury lamps doped with iron or gallium. The UV-light emitted from these types of light sources covers a wide range of wave lengths. However, the shortest wave lengths cause formation of non desired ozone and the long wave light, which is partly within the infra red range, generates
10 heat. Halogen lamps possess short service lifes in the order of 1000 hours compared to tens of thousands hours for UV-LED lamps. Therefore, UV-LED lamps are preferred in comparison to mercury lamps.

15 UV-LED lamps may be suitably arranged for obtaining optimum results. LED-lamps of different lengths may be used to allow for optimised UV-curing by individually adjusting the number of UV-LED units and their intensity levels. A possible production set up for rotational symmetric products is to place the
20 products to be UV-cured in an upright position, e.g. on a slowly rotating disc. Very short curing times may be obtained by using vertically positioned and adjustable UV-LED heads, e.g. three such heads uniformly spaced at 120 degrees angle, e.g. of the type Phoseon RX StarFire Max, with 365 nm wavelength, and
25 optionally additional UV-spot lamps, e.g. of the type Phoseon RX FireFlex units, above and below the mould to allow for simultaneously irradiation outer and internal parts. According to the present invention cure times in the order of 10 seconds are obtainable for thin walled products such as indoor cable
30 terminations (SOT).

In this sense, cable terminations, for indoor or outdoor use, or stress cones are manufacturable, as shaped articles in the sense of the present invention.

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After curing, the cured product can be taken out of the mould with conventional methods.

The UV-cured silicone compositions, cured according to the present invention, are preferably used as electrical insulations both for indoor and outdoor applications, hollow core insulators, cable accessories such as cable terminations, medium voltage (MV) and high voltage (HV) surge arresters, medium voltage (MV) vacuum interrupters or bushings.

UV curable silicone resin compositions are known and generally comprise at least an organopolysiloxane with at least one alkenyl group per molecule and at least one organohydrogenpolysiloxane. In order to activate the cross-linking reaction, i.e. the addition reaction between the alkenyl group ($-\text{CH}=\text{CH}_2$) and the $\equiv\text{SiH}$ -groups, the composition comprises a UV sensitive cross-linking catalyst.

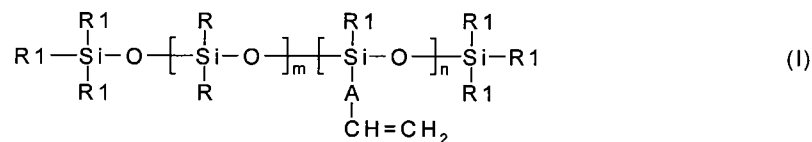
Preferred UV-curable silicone resin compositions are liquid to pasty and preferably contain (a) at least an organopolysiloxane with an average of at least two alkenyl groups per molecule, said polysiloxane being linear, branched or cyclic or a mixture of such polysiloxanes; (b) at least one organohydrogenpolysiloxane, preferably with an average of at least two $\equiv\text{SiH}$ -groups per molecule, said polysiloxane being linear, branched or cyclic or a mixture of such polysiloxanes, and (c) a catalytic amount of at least one UV-sensitive cross-linking catalyst.

The molar ratio of the of the $\equiv\text{SiH}$ -groups to the alkenyl groups present in the composition is within the range of about 1,5 : 4,5; preferably of 1,8 : 2,5; and preferably is at least 2.0.

The UV curable silicone resin compositions according to the present invention may contain further additives such as fillers, stabilizers, silicon oils, as known in the art.

Organopolysiloxane with an average of at least two alkenyl groups per molecule [component (a) as mentioned above], are known *per se*. Preferred such organopolysiloxanes correspond to compounds of formula (I) resp. to a mixture of compounds of

formula (II):



wherein

- 5 R independent of each other is (C₁-C₈)-alkyl or phenyl, preferably (C₁-C₄)-alkyl, preferably methyl;
- R₁ independent of each other has one of the meanings of R or is a residue of formula -A-CH=CH₂;
- A is a residue -(C_sH_{2s})_p-, preferably -[(CH₂)_s]_p-, wherein
- 10 s is 1 to 6, preferably 1;
- p is zero or one;
- m is zero to 5000, preferably an average value of 20 to 5000, preferably 50 to 1500;
- n is zero to 100, preferably an average number of 2 to 100,
- 15 preferably 2 to 20;
- wherein the compound of formula (I), resp. the mixture of compounds of formula (I), has an average of at least two alkenyl groups of the formula -A-CH=CH₂ per molecule, and the groups of the formulae -[Si(R)(R)O]- and -[Si(R₁)(A-CH=CH₂)O]- are arranged
- 20 in an arbitrary sequence.

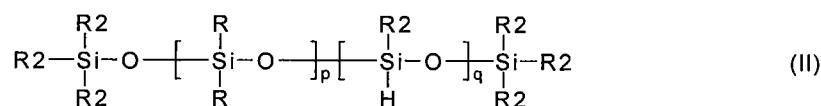
Compounds of formula (I) generally are a mixture of compounds of formula (I) with different molecular weights. This is known to the expert in the art. The alkenyl group [-A-CH=CH₂] can be for

25 example vinyl, allyl, 3-butenyl, 4-pentenyl, and preferably vinyl (i.e. p = zero). The terminal silyloxy groups preferably independent of each other stand for dimethylvinylsiloxy, wherein n preferably is zero.

30 The organopolysiloxanes of component (a) and preferably of formula (I) preferably have a viscosity within the range of 0.5 to 30'000 Pas, preferably within the range of 1 to 500 Pas, and preferably within the range of 1 to 100 Pas, measured according to DIN 53 019 at 20°C. The sum of [m + n] is preferably in the

average range of 20 to 5000, preferably within the average range of 50 to 1500.

Organopolysiloxane with an average of at least two $\equiv\text{SiH}$ -groups per molecule, [component (b) as mentioned above], are known per se. Preferably component (b) comprises at least a linear, branched or cyclic organohydrogenpolysiloxane with an average of at least two $\equiv\text{SiH}$ -groups per molecule and preferably corresponds to compound of formula (II) or a mixture of compounds of formula (II):



wherein

- R independent of each other is $(\text{C}_1\text{-C}_8)$ -alkyl or phenyl, preferably $(\text{C}_1\text{-C}_4)$ -alkyl, preferably methyl;
- R₂ independent of each other has one of the meanings of R or is hydrogen;
- p is zero to 5000, preferably an average value of 20 to 5000, preferably 50 to 1500;
- n is zero to 60, preferably an average number of 2 to 60, preferably 2 to 30;

wherein the compound of formula (II), resp. the mixture of compounds of formula (II), has an average of at least two $\equiv\text{SiH}$ -groups per molecule, and the groups of the formulae $-\text{[Si(R)(R)O]}-$ and $-\text{[SiH(R}_2\text{)O]}-$ are arranged in an arbitrary sequence.

Compounds of formula (II) generally are a mixture of compounds of formula (II) with different molecular weights. This is known to the expert in the art. The terminal silyloxy groups preferably independent of each other stand for dimethylhydrogen-siloxy, wherein q preferably is zero. The organopolysiloxanes of component (b) and of formula (II) preferably have a viscosity within the range of 0.1 to 5 Pas.

Component (b) may represent or comprise a cyclic organohydrogen-polysiloxane. In this case, two terminal substituents R_2 of two different terminals of the molecule form together an oxygen atom. The molecule of compound (II) in this case is composed of
5 $-\text{[Si(R)(R)O]}-$ units and of $-\text{[SiH(R}_2\text{)O]}-$ units or only of $-\text{[SiH(R}_2\text{)O]}-$ units, which form the ring structure. Such a cyclic molecule is composed preferably 4 to 8 of such units, preferably of an average of 4 of such units corresponding to the formula $[-\text{SiH(R}_2\text{)O-}]_4$.

10

The UV-curable silicone resin composition contains the UV sensitive hydrosilylation cross-linking catalyst in amounts within the range of 1 ppm to 5000 ppm, preferably within the range of 5 ppm to 1000 ppm, preferably 50 ppm to 200 ppm, and preferably
15 about 100 ppm, calculated to the weight of metal contained in the catalyst and the sum of the weight of component (a) and component (b).

The handling, treatment, mixing and application of the components of the UV curable silicone resin composition is known to
20 the expert in the art and needs nor further explanation.

Numerous UV-sensitive cross-linking catalysts are known in the art. Such UV-sensitive catalysts for effecting the addition of
25 silicone hydride compounds to vinyl-substituted silanes and siloxanes generally referred to as hydrosilylation of two-part silicone resin compositions, are preferably palladium and/or platinum catalysts.

UV sensitive cross-linking catalysts can be made from a metal, or more than one metal, of group VIII of the periodic system of elements, preferably from ruthenium (Ru), osmium (Os), cobalt (Co), rhodium (Rh), iridium (Ir), nickel (Ni), palladium (Pd) and platinum (Pt), and represent heterogeneous forms as well as
30 chemical compounds and complexes therefrom. Preferred are such forms made from rhodium, palladium and platinum, especially from
35

palladium and platinum, in heterogeneous forms or as chemical compounds or complexes thereof.

Preferred UV-sensitive cross-linking catalysts are heterogeneous forms of these metals, by using the metal *per se* or compositions wherein the metal is deposited on a carrier material, such as deposited on charcoal, silica or alumina, preferably on alumina and especially on gamma-alumina. As starting materials, for example H_2PtCl_6 , PdCl_6 or RhCl_6 are used and reduced to the metal, so that corresponding metal particles are deposited on the carrier material, with an average particle size which is preferably in nano-size range. Preferred are such heterogeneous platinum catalysts. Such catalysts are known in the art.

Preferred UV-sensitive cross-linking catalysts further are chemical compounds and complexes of metals of group VIII of the periodic system of elements, as mentioned above, used as homogeneous catalysts. Preferred are platinum(0) and platinum(II) compounds, e.g. in the form of complexes. Preferred platinum containing catalysts are chloroplatinic acid (H_2PtCl_6) in anhydrous form or as hexahydrate, or platinum Pt(0) or Pt(II) complexes which have ligands selected from halides, preferably chlorine; $(\text{C}_1\text{-C}_8)\text{alkyl}$ radicals; $(\text{C}_1\text{-C}_8)\text{aliphatic unsaturated}$ radicals, e.g. 1,5-cyclooctadiene (C_8H_{12}), such $(\text{C}_8\text{H}_{12})_2\text{PtCl}_2$, or styrene, yielding $(\text{styrene})_2\text{PtCl}_2$.

Preferred are also platinum complexes which are obtained by reacting chloroplatinic acid and complexes thereof with an aliphatic unsaturated organosilane or an aliphatic unsaturated organopolysiloxane compound, such as a vinylsilane or vinyl groups containing organopolysiloxane. Such hydrosilylation catalysts are described for example in US 4,681,963, US 4,705,765, or US 5,106,939, the contents of which are incorporated herein by reference.

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Examples for compounds to be used as UV-sensitive hydrosilylation cross-linking catalysts on the basis of palladium (Pd)

are Pd(0)-compounds such tetrakis(triphenylphosphino)palladium and the corresponding complexes with the ligands tri-(2-tolyl)-phosphine, tris-(2-furyl)phosphine, tris(tert.-butyl)phosphine, or the two-valent ligands dppm [1,1-bis(diphenylphosphino-methan)] or dppe [1,2-bis-(diphenylphosphino)ethane]. Pd(II)-compounds, such as PdCl₂, Pd(dppe)Cl₂, Pd(OAc)₂, Pd(dppe)(OAc)₂, π -allyl-Pd-complex, can also be used. Such analogous complexes made from metals of group VIII of the periodic system of elements, as mentioned above, preferably are made from ruthenium (Ru), osmium (Os), cobalt (Co), rhodium (Rh), iridium (Ir), nickel (Ni), palladium (Pd) and platinum (Pt), preferably made from palladium and platinum, and as analogous compounds made from platinum. Such compounds are known in the art and can be used within the scope of the present invention.

The UV-sensitive hydrosilylation cross-linking catalyst as defined herein above is added to the UV-curable silicone composition, so that said UV-curable silicone composition contains said UV-sensitive hydrosilylation cross-linking catalyst in amounts within the range of 0.1 parts per hundred (phr) to 3 phr, preferably within the range of 0.5 phr to 2.5 phr, preferably 0.5 phr to 1.5 phr, calculated to the weight of metal contained in the catalyst and the weight of the UV-curable silicone composition. These weight ratios, however, are not critical, and higher amounts may be added if indicated.

The following examples illustrate the invention.

Example 1

Stress relief cones were produced using a PMMA tube with a defined outer diameter of 50 mm to form the mould core on which the insert field grading Alfex tub was positioned. The PMMA tube was put into a multi-part mould comprising of two thermoformed mould-halves from PMMA sheets of about 4 mm that are fastened together. The PMMA tube and the thermoformed mould were kept in place with a metal frame. Inlets were mounted onto the PMMA tube at the narrow extremity of the cone. UV curable silicone (e.g.

UV Electro 235-2 from Momentive) was injected into the transparent mould starting from the narrow part of the cone. Once the mould was filled a thin layer of silicone flew between the PMMA tube and the field grading Alfex tube, ensuring a continuity in the geometry (no electrical triple points). UV light was then applied by rotating the stress relief cone in front of a UV LED lamp RX Starfire. The whole stress cone was cured within 5 to 10 minutes. The metal frame was removed and air was inserted between the mould and the cured part to ensure easy demoulding. The same procedure was used to remove the PMMA tube from the moulded part.

Example 2

Two mould halves were manufactured by thermoforming a PMMA plate with a wall thickness of 8 mm. The inner geometry of the two mould halves was corresponding to the external shape of a silicone embedded vacuum interrupter. On one of the mould halves, an inlet was mounted for the injection of the liquid silicone rubber. A vacuum interrupter was placed between the two thermoformed mould halves and the mould was closed with bolts. The UV curable silicone (e.g. UV Electro 235-2 from Momentive) was then injected into the PMMA mould via the inlet. Once the mould was filled, it was rotated in front of a UV LED lamp RX StarFire at a speed of 6 rpm. The distance between the mould and the lamp was ca. 1 cm. After an illumination time of 2 minutes, the silicone was cured and the part could be demoulded.

Example 3

Two mould halves were manufactured by thermoforming a PMMA plate with a wall thickness of 3 mm. The inner geometry of the two mould halves was corresponding to the external shape of a silicone embedded vacuum interrupter. On one of the mould halves, an inlet was mounted for the injection of the liquid silicone rubber. A vacuum interrupter was placed between the two thermoformed mould halves and the mould was closed with bolts. The UV curable silicone (e.g. UV Electro 235-2 from Momentive) was then injected into the PMMA mould via the inlet. Once the

mould was filled, it was rotated in front of a UV LED lamp RX StarFire at a speed of 6 rpm. The distance between the mould and the lamp was ca. 1 cm. After an illumination time of 2 minutes, the silicone was cured and the part could be demoulded.

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All elements, parts and steps described herein are preferably included. It is to be understood that any of these elements, parts and steps may be replaced by other elements, parts and steps or deleted all together as will be obvious to those

10 skilled in the art.

Broadly this writing has disclosed at least the following.

Method of producing a shaped article from a UV-curable silicone rubber composition by irradiating said UV-curable silicone

15 rubber composition with UV-light, comprising the steps of (i)

filling a UV-curable silicone rubber composition into a thermoformed UV-transparent mould which is made from a thermoplastic

UV-transparent polymer, and (ii) curing said UV-curable silicone rubber composition within said thermoformed UV-transparent mould

20 by irradiation with UV-light; said shaped articles being in the form of an electrical insulator for indoor and outdoor use; and electrical articles comprising an electrical insulation made by the method according to the present invention.

25 This writing has disclosed at least the following broad concepts.

Concept 1. Method of producing a shaped article from a UV-curable silicone rubber composition by irradiating said UV-curable silicone rubber composition with UV-light, characterized

30 by the steps of filling a UV-curable silicone rubber composition into a thermoformed UV-transparent mould which is made from a thermoplastic UV-transparent polymer, and

curing said UV-curable silicone rubber composition within said thermoformed UV-transparent mould by irradiation with UV-

35 light.

Concept 2. Method according to concept 1, characterized in that said shaped articles are electrical insulators for indoor and outdoor use, preferably high voltage electrical insulators.

- 5 Concept 3. Method according to concept 1 or 2, characterized in that said thermoformed UV-transparent mould is entirely made from a thermoplastic UV-transparent polymer and preferably entirely made from a thermoplastic UV-transparent and UV-stable polymer.

10

Concept 4. Method according to concept 3, characterized in that said UV-transparent polymer is selected from the group comprising polymethylmethacrylate; polyvinylchloride; cyclo-

- 15 polycarbonate; polyethylene-terephthalate; styrene-acrylonitrile polymers; polysulfone polymers; polymethacrylimide polymers; polypropylene; and polystyrene.

- Concept 5. Method according to concept 3, characterized in that
20 said UV-transparent polymer is selected from the group comprising polymethylmethacrylate; polyvinylchloride; cyclo-olefine-polymers; polymethylacryl-methylimide-polymers; polycarbonate; and polyethylene-terephthalate; preferably from polymethylmethacrylate and and polyvinylchloride.

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Concept 6. Method according to any one of the concept 1-5, characterized in that said UV-transparent polymer has a UV-transparency of at least 30%, preferably of at least 60%, preferably of at least 80%, and preferably of at least 90%.

30

Concept 7. Method according to any one of the concept 1-6, characterized in that the wall thickness of the mould is between about 1 mm and 50 mm.

- 35 Concept 8. Method according to concept 7, characterized in that the wall thickness of the mould is higher than 1 mm and is produced from planar sheet material that has been thermoformed

in order to form a negative or a positive of the article to be shaped.

5 Concept 9. Method according to concept 7 or 8, characterized in that the wall thickness of the mould is within the range of about 2.0 mm to about 60 mm, preferably within the range of about 3.0 mm to about 50 mm, preferably within the range of about 3.0 mm to about 40 mm, preferably within the range of about 3.0 mm to about 30 mm.

10

Concept 10. Method according to any one of the concept 1-7, characterized in that the light source for irradiation with UV-light has a wavelength within the range of 180 nm to 700 nm, preferably within the range of 190 nm to 500 nm, preferably
15 within the range of 300 nm to 400 nm, preferably at about 360 nm to 400 nm.

Concept 11. Method according to any one of the concept 1-10, characterized in that the UV-light source is an arcing UV-lamp, or a microwave powered UV-lamp or is based on UV-LED technique, preferably is a UV-light source based on UV-LED technique, preferably in the form of a Semiconductor Light Matrix (SLM), as closed packed LED's.

25 Concept 12. Method according to any one of the concept 1-11, characterized in that the UV-light-irradiation intensity applied for UV-curing is within the range of 1 W/cm² to 4 W/cm², preferably within the range of 2 W/cm² to 4 W/cm².

30 Concept 13. Method according to any one of the concept 1-12, characterized in that the UV-curable silicone resin composition is liquid to pasty and contain (a) at least an organopolysiloxane with an average of at least two alkenyl groups per molecule, said polysiloxane being linear, branched or cyclic or
35 a mixture of such polysiloxanes; (b) at least one organohydrogenpolysiloxane, with an average of at least two $\equiv\text{SiH}$ -groups per molecule, said polysiloxane being linear, branched or

cyclic or a mixture of such polysiloxanes, and (c) a catalytic amount of at least one UV-sensitive cross-linking catalyst.

5 Concept 14. Method according to concept 13, characterized in that the molar ratio of the of the $\equiv\text{SiH}$ -groups to the alkenyl groups present in the composition is within the range of 1,5 : 4,5; preferably of 1,8 : 2,5; and preferably is at least 2.0.

10 Concept 15. Method according to concept 13, characterized in that the UV sensitive cross-linking catalysts is made from a metal of group VIII of the periodic system of elements, preferably from ruthenium (Ru), osmium (Os), cobalt (Co), rhodium (Rh), iridium (Ir), nickel (Ni), palladium (Pd) and platinum (Pt), and represent heterogeneous forms as well as chemical
15 compounds and complexes thereof.

Concept 16. Method according to concept 13, characterized in that the UV sensitive cross-linking catalysts is made from rhodium, palladium and platinum, preferably from palladium and
20 platinum, in heterogeneous forms or as a chemical compound or a complex thereof.

Concept 17. Method according to any one of the concept 13-16, characterized in that the UV-curable silicone resin composition
25 contains the UV sensitive hydrosilylation cross-linking catalyst in amounts within the range of 1 ppm to 5000 ppm, preferably within the range of 5 ppm to 1000 ppm, preferably 50 ppm to 200 ppm, and preferably about 100 ppm, calculated to the weight of metal contained in the catalyst and the sum of the weight of
30 component (a) and component (b).

Concept 18. Method according to any one of the concept 1-17, characterized in that the UV curable silicone resin composition contains further additives selected from fillers, stabilizers,
35 and silicon oils.

Concept 19. Shaped articles in the form of an electrical insulator for indoor and outdoor use, preferably as a high voltage electrical insulator, made by the method according to any one of the claims 1-18.

5

Concept 20. Shaped articles according to concept 19 in the form of an electrical insulator as hollow core insulators, cable accessories, preferably cable terminations, medium voltage (MV) and high voltage (HV) surge arresters, medium voltage (MV)

10 vacuum interrupters or bushings.

Concept 21. Electrical articles comprising an electrical insulation made by the method according to any one of the concepts 1-18.

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Concept 22. A thermoformed UV-transparent mould which is made from a thermoplastic UV-transparent polymer and which preferably is made from a thermoplastic UV-transparent and UV-stable polymer for carrying out the method as claimed according to any

20 one of the concepts 1-18.

Claims

1. Method of producing a shaped article from a UV-curable silicone rubber composition by irradiating said UV-curable silicone rubber composition with UV-light, characterized by the steps of (i) filling a UV-curable silicone rubber composition into a thermoformed UV-transparent mould which is made from a thermoplastic UV-transparent polymer, and (ii) curing said UV-curable silicone rubber composition within said thermoformed UV-transparent mould by irradiation with UV-light.
2. Method according to claim 1, characterized in that said shaped articles are electrical insulators for indoor and outdoor use, preferably high voltage electrical insulators.
3. Method according to claim 1 or 2, characterized in that said thermoformed UV-transparent mould is entirely made from a thermoplastic UV-transparent polymer and preferably entirely made from a thermoplastic UV-transparent and UV-stable polymer.
4. Method according to claim 3, characterized in that said UV-transparent polymer is selected from the group comprising polymethylmethacrylate; polyvinylchloride; cyclo-olefine-polymers; polymethylacryl-methylimide-polymers; polycarbonate; polyethylene-terephthalate; styrene-acrylonitrile polymers; polysulfone polymers; polymethacrylimide polymers; polypropylene; and polystyrene.
5. Method according to claim 3, characterized in that said UV-transparent polymer is selected from the group comprising polymethylmethacrylate; polyvinylchloride; cyclo-olefine-polymers; polymethylacryl-methylimide-polymers; polycarbonate; and polyethylene-terephthalate; preferably from polymethylmethacrylate and polyvinylchloride.
6. Method according to any one of the claims 1-5, characterized in that said UV-transparent polymer has a UV-transparency

of at least 30%, preferably of at least 60%, preferably of at least 80%, and preferably of at least 90%.

7. Method according to any one of the claims 1-6, characterized in that the wall thickness of the mould is between about 1 mm and 50 mm.

8. Method according to claim 7, characterized in that the wall thickness of the mould is higher than 1 mm and is produced from planar sheet material that has been thermoformed in order to form a negative or a positive of the article to be shaped.

9. Method according to claim 7 or 8, characterized in that the wall thickness of the mould is within the range of about 2.0 mm to about 60 mm, preferably within the range of about 3.0 mm to about 50 mm, preferably within the range of about 3.0 mm to about 40 mm, preferably within the range of about 3.0 mm to about 30 mm.

10. Method according to any one of the claims 1-7, characterized in that the light source for irradiation with UV-light has a wavelength within the range of 180 nm to 700 nm, preferably within the range of 190 nm to 500 nm, preferably within the range of 300 nm to 400 nm, preferably at about 360 nm to 400 nm.

11. Method according to any one of the claims 1-10, characterized in that the UV-light source is an arcing UV-lamp, or a microwave powered UV-lamp or is based on UV-LED technique, preferably is a UV-light source based on UV-LED technique, preferably in the form of a Semiconductor Light Matrix (SLM), as closed packed LED's.

12. Method according to any one of the claims 1-11, characterized in that the UV-light-irradiation intensity applied for UV-curing is within the range of 1 W/cm² to 4 W/cm², preferably within the range of 2 W/cm² to 4 W/cm².

13. Method according to any one of the claims 1-12, characterized in that the UV-curable silicone resin composition is liquid to pasty and contain (a) at least an organopolysiloxane with an average of at least two alkenyl groups per molecule, said polysiloxane being linear, branched or cyclic or a mixture of such polysiloxanes; (b) at least one organohydrogenpoly-
5 siloxane, with an average of at least two $\equiv\text{SiH}$ -groups per molecule, said polysiloxane being linear, branched or cyclic or a mixture of such polysiloxanes, and (c) a catalytic amount of
10 at least one UV-sensitive cross-linking catalyst.

14. Method according to claim 13, characterized in that the molar ratio of the of the $\equiv\text{SiH}$ -groups to the alkenyl groups present in the composition is within the range of 1,5 : 4,5;
15 preferably of 1,8 : 2,5; and preferably is at least 2.0.

15. Method according to claim 13, characterized in that the UV sensitive cross-linking catalysts is made from a metal of group VIII of the periodic system of elements, preferably from
20 ruthenium (Ru), osmium (Os), cobalt (Co), rhodium (Rh), iridium (Ir), nickel (Ni), palladium (Pd) and platinum (Pt), and represent heterogeneous forms as well as chemical compounds and complexes thereof.

25 16. Method according to claim 13, characterized in that the UV sensitive cross-linking catalysts is made from rhodium, palladium and platinum, preferably from palladium and platinum, in heterogeneous forms or as a chemical compound or a complex thereof.

30 17. Method according to any one of the claims 13-16, characterized in that the UV-curable silicone resin composition contains the UV sensitive hydrosilylation cross-linking catalyst in amounts within the range of 1 ppm to 5000 ppm, preferably within
35 the range of 5 ppm to 1000 ppm, preferably 50 ppm to 200 ppm, and preferably about 100 ppm, calculated to the weight of metal

contained in the catalyst and the sum of the weight of component (a) and component (b).

18. Method according to any one of the claims 1-17, characterized in that the UV curable silicone resin composition contains further additives selected from fillers, stabilizers, and silicon oils.

19. Shaped articles in the form of an electrical insulator for indoor and outdoor use, preferably as a high voltage electrical insulator, made by the method according to any one of the claims 1-18.

20. Shaped articles according to claim 19 in the form of an electrical insulator as hollow core insulators, cable accessories, preferably cable terminations, medium voltage (MV) and high voltage (HV) surge arresters, medium voltage (MV) vacuum interrupters or bushings.

21. Electrical articles comprising an electrical insulation made by the method according to any one of the claims 1-18.

22. A thermoformed UV-transparent mould which is made from a thermoplastic UV-transparent polymer and which preferably is made from a thermoplastic UV-transparent and UV-stable polymer for carrying out the method as claimed according to any one of the claims 1-18.

Fig. 1

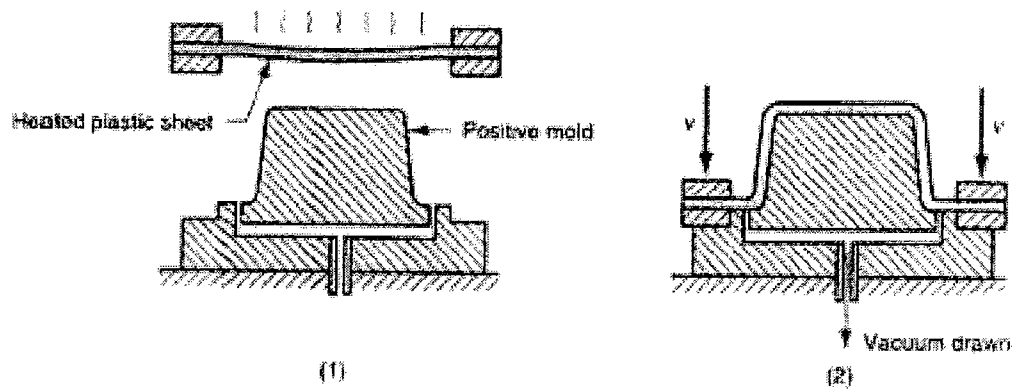
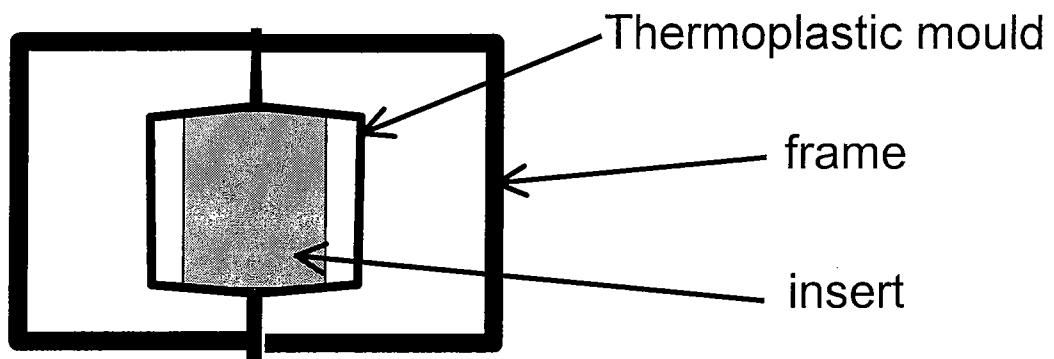


Fig. 2



A. CLASSIFICATION OF SUBJECT MATTER*B29C 35/08(2006.01)i, B29C 39/00(2006.01)i, C08J 3/28(2006.01)i, C08L 83/04(2006.01)i, C08G 77/08(2006.01)i*

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)

B29C 35/08; C08K 5/56; C08L 83/04; B29D 11/00; H01L 21/00

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 2008-0033071 A1 (UWE IRMER et al.) 07 February 2008 See paragraph [238]; claims 27-52	1-3 4-5
X Y	US 2008-0290534 A1 (YIN CHANGHONG et al.) 27 November 2008 See [23], [24], [32]; claims 1-20	1,3-5 4-5
A	US 2003-0122269 A1 (STEVEN WEBER et al.) 03 July 2003 See the whole document	1-5
A	US 7923272 B2 (LEE HWANG-PAO) 12 April 2011 See the whole document	1-5



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"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

"&" document member of the same patent family

Date of the actual completion of the international search

15 FEBRUARY 2012 (15.02.2012)

Date of mailing of the international search report

17 FEBRUARY 2012 (17.02.2012)

Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2011/039339**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 8,14-16,20
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
The said claims refer to claims that are not drafted in accordance with the second and third sentences of Rule 6.4(a).
3. ☒ Claims Nos.: 6,7,9-13,17-19,21,22
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2011/039339

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008-0033071 A1	07.02.2008	AT 444331 T CN 101039999 A0 DE 102004036573 A1 DE 502005008253 D1 EP 1817372 A1 EP 1817372 B1 ES 2333138 T3 JP 2008-508382 A JP 2008-508382 T KR 10-2007-0041764 A KR20070041764A KR20070041764A WO 2006-010763 A1	15.10.2009 19.09.2007 23.03.2006 12.11.2009 15.08.2007 30.09.2009 17.02.2010 21.03.2008 21.03.2008 19.04.2007 19.04.2007 19.04.2007 02.02.2006
US 2008-0290534 A1	27.11.2008	AU 2008-242679 A1 CA 2684870 A1 CN 101663158 A EP 2152503 A1 JP 2010-524729 A KR 10-2010-0017185 A TW 200912424 A WO 2008-131329 A1	30.10.2008 30.10.2008 03.03.2010 17.02.2010 22.07.2010 16.02.2010 16.03.2009 30.10.2008
US 2003-0122269 A1	03.07.2003	US 6890458 B2	10.05.2005
US 7923272 B2	12.04.2011	US 2010-0041169 A1	18.02.2010