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(54) Title: ARTICLE/PART COMPRISING A POLYMERIC COMPONENT AND A METALLIC COATING

(57) Abstract: The invention pertains to a article or a part, comprising: - a first layer (1) of a composition (C) comprising at least one poly(ether ether ketone)-poly(ether diphenyl ether ketone) (PEEK-PEDEK) copolymer, wherein the composition (C) has a melting temperature (Tm) of at least 290°C, as measured by differential scanning calorimetry (DSC) according to ASTM D3418, and - at least one coating (2) of metal having a thickness of at least 20 pm, preferably at least 30 pm. The present invention also relates to a process for preparing this article/part by metallisation and to the use of such articles and parts in electrical & electronic applications, mobile electronics, smart devices & wearables and smart phones.

Description

Article/part comprising a polymeric component and a metallic coating

Related applications

[0001] This application claims priority to US Provisional Appl No. 62/697,610 filed on July 13, 2018, and to European patent application No 18189542.6 filed on August 17, 2018, the whole content of these applications being incorporated herein by reference for all purposes.

Technical Field

[0002] The present disclosure relates to a article or a part, comprising:
- a first layer (1) of a composition (C) comprising at least one poly(ether ether ketone)-poly(ether diphenyl ether ketone) (PEEK-PEDEK) copolymer, wherein the composition (C) has a melting temperature (Tm) of at least 290°C, as measured by differential scanning calorimetry (DSC) according to ASTM D3418, and
- at least one coating (2) of metal having a thickness of at least 30 pm, preferably at least 40 pm.

[0003] The present invention also relates to a process for preparing this article/part by metallisation and to the use of such articles and parts in electrical & electronic applications, mobile electronics, smart devices & wearables and smart phones.

Background Art

[0004] There is a high demand for the production of metallic coatings in various industrial sectors, from simple operations such aesthetic layers to more complex applications like electronic devices. Coatings of various types are frequently applied on parts to protect against hostile environments, to enhance their performance and durability, but also for aesthetic reasons. When considering the manufacturing of metallic coatings on surfaces, thermal spray methods are widely used for industrial applications. In such processes, the feedstock metal, typically in the form of powder or wire, is

heated to melting point and propelled as individual droplets towards the working surface. The energy required for the melting process is usually generated by combustible gases or an electric arc. As the particles impinge on the substrate, they splat (deform) and solidify.

[0005] Physical Vapor Deposition (PVD) is one of the available metallization methods. High temperature PVD is a cost effective way of shielding articles or parts, for examples with unique geometries. PVD metallization process also offers the advantages of a high throughtput and a metal coating of a significant thickness.

[0006] Due to their cost and ease of processing/shaping, polymeric materials are widely used. They however present a certain number of weaknesses for certain industries, for example erosion, swelling, warpage, porosity and susceptibility to certain fluids. Applying metal coatings or layers to the surface of polymer articles/parts is of considerable commercial importance because of the desirable properties obtained by combining polymers and metals.

[0007] Several prior art documents describe polymer-metal hydrib articles and methods for obtaining these articles.

[0008] US 9,909,207 describes a process for the deposition of aluminum on to non-metallic and composite substrates, such as polyether ether ketone (PEEK) or polyether ketone ketone (PEKK), wherein the non-metallic and composite substrates have opposing first and second sides. The substrate is inserted into a stream of ions and vapor of the coating with a first side of the substrate facing a first electric grid. The substrate is at the same voltage potential as the first electric grid and a primer coating is deposited on the first side. The primer coated first side is next coated to a desired thickness by insertion into the ion stream with the substrate at a negative potential relative to the first grid. The substrate is then rotated so the second side is facing the first grid with the substrate at a negative potential relative the first grid for a time effective to deposit the coating to a desired thickness.

[0009] US 2012/0237789 relates to metal-clad polymer article comprising a polymeric material defining a substrate and a metallic material covering at

least part of a surface of said polymeric material, said metallic material having a microstructure and presenting a thickness between 10 and 500 microns. The article may comprise an intermediate layer between said polymeric material and said metallic material. The polymeric material may be epoxy resins, phenolic resins, polyester resins, urea resins, melamine resins, thermoplastic polymers, polyolefins, polyethylenes, polypropylenes, polyamides, poly-ether-ether-ketones, poly-aryl-ether-ketones, poly ether ketones, poly-ether-ketone-ketones, mineral filled polyamide resin composites, polyphthalamide, polyphtalates, polystyrene, polysulfone, polyimides, neoprenes, polyisoprenes, polybutadienes, polyisoprenes, polyurethanes, butadiene-styrene copolymers, chlorinated polymers, polyvinyl chloride, fluorinated polymers, polytetrafluoroethylene, polycarbonates, polyesters, liquid crystal polymers, partially crystalline aromatic polyesters based on p-hydroxybenzoic acid, polycarbonates, acrylonitrile-butadiene-styrene their copolymers and their blends.

[0010] US 6,074,740 relates to a metallized plastics part based on a multiphase polymer mixture comprising a thermoplastic polymer A having a melting point of more than 100°C and a polymeric filler B that promotes adhesion of a metal coat to the polymer mixture, and wherein the polymeric filler is at least one selected from the group consisting of polyarylene sulfide, oxidized polyarylene sulfide, polyimide, aromatic polyester and polyether ketone and a metal coat adhered to the polymer mixture.

[001 1] WO 2018/024744 describes polymer-metal junctions, which are made by contacting a PEEK-PEDEK copolymer with a metal surface, preferably a structured metal surface, more preferably a nano-structured metal surface, most preferably an NMT-treated metal surface. As an example, the polymer composition is deposited on or over-molded onto the metal surface using any suitable meltprocessing and deposition method. In particular, the polymer-metal junction may be made by injection or compression molding the polymer composition onto the metal surface. This document does not describe a metal-coating.

[0012] One of the fundamental limitations associated with the PVD process is the lack of available polymer materials which can wistand the temperature used in the PVD process, generally above 250°C.

[0013] Poly(aryl ether ketone) polymers (PAEK) are a class of polymers that can be subjected to high temperatures for the duration of the PVD process without suffering degradation. However, the Applicant has notificed that PAEK polymers can suffer from other processing issues such as warpage which impacts the dimensional stability of the molded part.

[0014] There is therefore a need for polymeric part material to be used in high temperature metallization processes, which makes possible the manufacture of metal-coated polymeric articles/parts with an improved set of mechanical and aesthetic properties, notably with improved dimensional

Summary of invention

[0015] An aspect of the present disclosure is directed to an article or a part, comprising:

- a first layer (1) of a composition (C) comprising at least one poly(ether ether ketone)-poly(ether diphenyl ether ketone) (PEEK-PEDEK) copolymer, wherein the composition (C) has a melting temperature (Tm) of at least 290°C, as measured by differential scanning calorimetry (DSC) according to ASTM D3418, and
- at least one coating (2) of metal having a thickness of at least 20 pm, preferably at least 30 pm, and more preferably at least 40 pm.

[0016] The applicant has found that the use of comprising at least one poly(ether ether ketone)-poly(ether diphenyl ether ketone) (PEEK-PEDEK) copolymer is advantageous as the base of an article or part to be metallized by a process using high temperatures, e.g. above 250°C, for example PVD.

[0017] Another aspect of the invention is a process for preparing the article/part of the invention, by metallisation of an article/part comprising a first layer of a composition (C) which comprises a polymeric component comprising at least one poly(ether ether ketone)-poly(ether diphenyl ether ketone) (PEEK-PEDEK) copolymer, wherein the composition (C) has a melting

temperature (Tm) of at least 290°C, as measured by differential scanning calorimetry (DSC) according to ASTM D3418. The metallisation may be performed by physical vapor deposition (PVD) in a high vaccum environment using thermal evaporation equipment. The article/part may be:

- etched using a chemical solution before metal deposition,
- polished before or after metal deposition,
- colored before or after metal deposition, and/or
- anodized after metal deposition.

[0018] Another aspect of the invention is the use of the article/part of the invention, for electrical & electronic applications, mobile electronics, smart devices & wearables and smart phones.

Description of embodiments

[0019] The present invention relates to an article or a part, comprising:

- a first layer (1) of a composition (C) comprising at least one poly(ether ether ketone)-poly(ether diphenyl ether ketone) (PEEK-PEDEK) copolymer, wherein the composition (C) has a melting temperature (Tm) of at least 290°C, as measured by differential scanning calorimetry (DSC) according to ASTM D3418, and
- at least one coating (2) of metal having a thickness of at least 20 pm, preferably at least 30 pm, and more preferably at least 40 pm.

[0020] The merit of the applicant has been to identify a composition of matter, also called hereby composition (C), which can wistand the high temperatures, for example above 250°C, used in metallization processes, such as PVD, and makes possible the manufacture of metallized articles or parts with improved dimensional stability.

[0021] The composition is such that it comprises at least one poly(ether ether ketone)-poly(ether diphenyl ether ketone) (PEEK-PEDEK) copolymer, and that it has a melting temperature (Tm) of at least 290°C, as measured by differential scanning calorimetry (DSC) according to ASTM D3418.

[0022] The present invention is in fact based on a poly(ether ether ketone)-poly(ether diphenyl ether ketone) (PEEK-PEDEK) copolymer as the main element of the composition (C), to build the first layer of the metallized article or part. This composition presents a high melting temperature (Tm), at least 290°C, as measured by differential scanning calorimetry (DSC) according to ASTM D3418, for example at least 300°C or at least 310°C.

[0023] Composition (C)

[0024] The composition (C) of the present invention constitutes the first layer (1) of the article or part, to be metallized with a layer of metal. The composition (C) is such that it comprises at least one poly(ether ether ketone)-poly(ether diphenyl ether ketone) (PEEK-PEDEK) copolymer, and that it has a melting temperature (Tm) of at least 290°C. The melting point (Tm) of the composition (C) is hereby measured using differential scanning calorimetry (DSC) according to ASTM D3418 employing a heating and cooling rate of 20°C/min.

[0025] The thickness of the first layer (1) may range from 100 pm to 5 cm, for example from 500 pm to 3 cm or from 1 mm to 1 cm.

[0026] The composition (C) comprises a polymeric component, and may also comprise at least another component, for example glass fibers. The composition (C) may also comprise several additional components, for example glass fibers and additive(s).

The composition (C) comprises at least one poly(ether ether ketone)-poly(ether diphenyl ether ketone) (PEEK-PEDEK) copolymer. It may also comprise additional polymers, for example selected from the group consisting of poly(aryl ether ketone) (PAEK), poly(aryl ether sulfone) (PAES), polyimides and polyamides.

[0027] The composition (C) may comprise at least one poly(ether ether ketone)-poly(ether diphenyl ether ketone) (PEEK-PEDEK) copolymer, based on the total weight of the polymeric component of the composition (C).

[0028] As explained above, the composition (C) of the invention may include other components. The composition (C) may for example comprise at least one additional component, for example selected from the group

consisting of fillers, colorants, lubricants, plasticizers, stabilizers, flame retardants, nucleating agents and combinations thereof. Fillers in this context can be reinforcing or non-reinforcing in nature.

[0029] Suitable fillers include calcium carbonate, magnesium carbonate, glass fibers, graphite, carbon black, carbon fibers, carbon nanofibers, graphene, graphene oxide, fullerenes, talc, wollastonite, mica, alumina, silica, titanium dioxide, kaolin, silicon carbide, zirconium tungstate, boron nitride and combinations thereof.

[0030] In embodiments that include fillers the concentration of the fillers in the part material ranges from 0.5 wt.% to 50 wt.%, with respect to the total weight of the composition (C). In these embodiments, the composition (C) may comprise, based on the total weight of the composition (C):

- from 0.5 wt.% to 50 wt.%, of fillers, for example glass fibers, for example from 1 to 40 wt.%, from 2 to 30 wt.% or from 5 to 20 wt.%; and
- from 50 to 99.5 wt.% of the polymeric component, as defined above, for example from 60 to 99 wt.%, from 70 to 98 wt.% or from 80 to 95 wt.%.

[0031] Glass fibers are silica-based glass compounds that contain several metal oxides which can be tailored to create different types of glass. The main oxide is silica in the form of silica sand; other oxides, such as oxides of calcium, sodium and aluminium, are incorporated to reduce the melting temperature and impede crystallization. Glass fibers may have a round cross-section or a non-circular cross-section (so called “flat glass fibers”), including oval, elliptical or rectangular. The glass fibers may be added as endless fibers or as chopped glass fibers, whereas chopped glass fibers are preferred. The glass fibers have generally a diameter of 5 to 20 pm preferably of 5 to 15 pm and more preferably of 5 to 10 pm.

[0032] According to an embodiment, the composition (C) comprises E-glass fibers.

[0033] According to another embodiment, the composition (C) comprises high modulus glass fibers having an elastic modulus (also called tensile modulus of elasticity) of at least 76, preferably at least 78, more preferably at least 80, and most preferably at least 82 GPa as measured according to ASTM D2343.

[0034] According to an embodiment, the composition (C) comprises high modulus glass fibers selected from the group consisting of R, S and T glass fibers. They are notably described in Fiberglass and Glass Technology, Wallenberger, Frederick T.; Bingham, Paul A. (Eds.), 2010, XIV. R, S and T glass fibers are composed essentially of oxides of silicon, aluminium and magnesium. In particular, R, S and T glass fibers comprise typically from 62-75 wt. % of S1O2, from 16-28 wt. % of AI2O3 and from 5-14 wt. % of MgO. Additionally, R, S and T glass fibers generally comprise less than 10 wt. % of CaO.

[0035] The composition (C) may comprise glass fibers in an amount of at least 1 wt. %, for example at least 3 wt. %, at least 5 wt. %, at least 8 wt. %, at least 10 wt. %, at least 12 wt. %, or at least 15 wt. %, based on the total weight of the composition (C).

[0036] The polymer composition (C1) may comprise glass fibers in an amount of less than 50 wt. %, for example less than 40 wt. %, less than 30 wt. %, less than 25 wt. %, less than 20 wt. %, less than 18 wt. %, or less than 17 wt. %, based on the total weight of the polymer composition (C1).

[0037] Preferably, the polymer composition (C1) may comprise glass fibers in an amount ranging from 1 to 50 wt. %, for example from 2 to 38 wt. %, from 4 to 28 wt. % or from 5 to 22 wt. %, based on the total weight of the polymer composition (C1).

[0038] According to one embodiment, the composition (C) comprises:

- from 50 to 100 wt.% of at least one poly(ether ether ketone)-poly(ether diphenyl ether ketone) (PEEK-PEDEK) copolymer, and
- from 0 to 50 wt.% of glass fibers and/or at least one additional component, for example selected from the group consisting of fillers, colorants, lubricants, plasticizers, flame retardants, nucleating agents and stabilizers,

based on the total weight of the composition (C).

[0039] According to another embodiment, the composition (C) consists essentially of:

- from 50 to 100 wt.%, from 65 to 99.1 wt.% or from 75 to 99.5 wt, % of at least one poly(ether ether ketone)-poly(ether diphenyl ether ketone)

(PEEK-PEDEK) copolymer, based on the total weight of the polymeric component, and

- from 0 to 50 wt.%, from 0.1 to 35 wt.% or from 0.5 to 25 wt.% of glass fibers and/or at least one additional component selected from the group consisting of fillers, colorants, lubricants, plasticizers, flame retardant, nucleating agent and stabilizers,

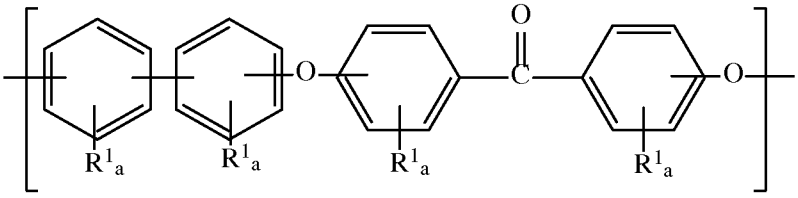
based on the total weight of the composition (C).

[0040] PEEK-PEDEK copolymer

[0041] As used herein, a PEEK-PEDEK or equivalently in the context of the present invention a PEDEK-PEEK copolymer denotes a polymer comprising repeat units (RPEDEK) and repeat units (RPEEK).

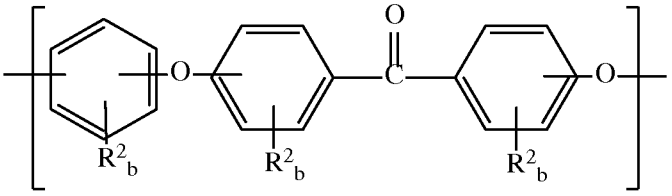
[0042] In some embodiments, the total number of repeat units (RPEDEK) and (RPEEK) in the PEEK-PEDEK copolymer is at least 50 mol.%, at least 60 mol.%, at least 70 mol.%, at least 80 mol.%, at least 90 mol.%, at least 95 mol.%, and most preferably at least 99 mol. %, relative to the total number of repeat units in the PEEK-PEDEK copolymer.

[0043] Repeat units (RPEDEK) may be represented by formula:



(A).

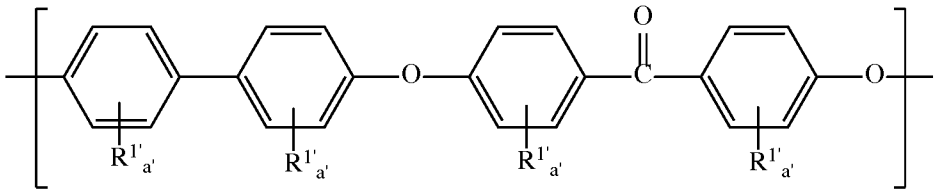
[0044] Repeat units (RPEEK) may be represented by formula :



(B).

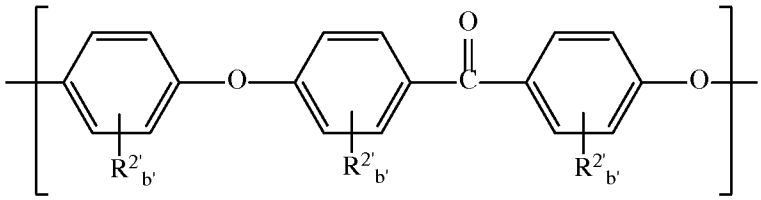
[0045] In formulas (A) and (B), each R^1 and R^2, equal to or different from each other, is independently at each occurrence selected from the group consisting of halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary ammonium; and each a and b is independently selected from the group consisting of integers ranging from 0 to 4.

[0046] According to an embodiment, repeat units (RPEDEK) are selected from units of formula :



(A-1).

[0047] According to another embodiment, repeat units (RPEEK) are selected from units of formula:

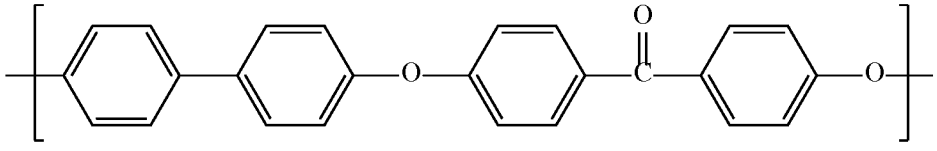


(B-1).

[0048] In formulas (A-1) and (B-1), each $R^{1'}$ and $R^{2'}$, equal to or different from each other, is independently at each occurrence selected from the group consisting of halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary ammonium; and each a' and b' is independently selected from the group consisting of integers ranging from 0 to 4.

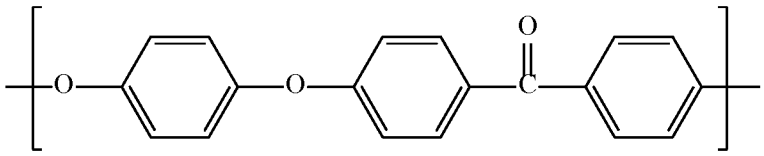
[0049] According to an preferred embodiment, the PEDEK-PEEK copolymer of the present invention denotes a polymer comprising at least 50 mol.%, collectively, of repeat units (RPEDEK) of formula (A-1) and repeat units (RPEEK) of formula (B-1).

[0050] In some embodiments, each a is zero in formula (A) or each a' is zero in formula (A'), which means that the repeat units (RPEDEK) are not substituted:



(A-2).

[0051] In some embodiments, each b is zero or each b' is zero, which means that the repeat units (RPEEK) are not substituted:

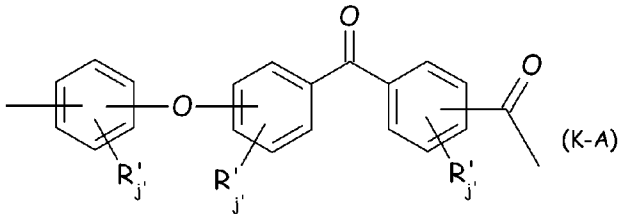


(B-2).

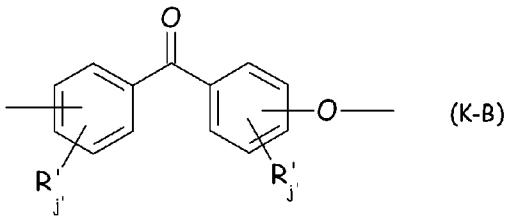
[0052] Preferably, repeat units (RPEDEK) are repeat units of formula (A-2), and repeat units (RPEEK) are repeat units of formula (B-2).

[0053] The PEEK-PEDEK copolymer of the present invention may additionally comprise repeat units (RPAEK) different from repeat units (RPEDEK) and (RPEEK), as above detailed. In such case, the amount of repeat units (RPAEK) my be comprised between 0.1 and 50 mol.%, for example 0.2 to 40 mol.% with respect to the total number of moles of repeat units of PEEK-PEDEK copolymer.

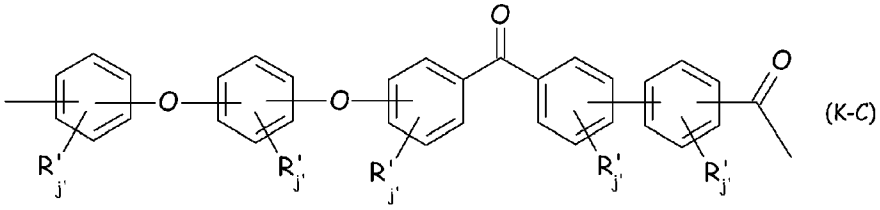
[0054] In some embodiments, the PEEK-PEDEK copolymer includes repeat units (RPAEK) different from repeat units (RPEEK) and (RPEDEK). Repeat units (RPAEK) may for example be selected from the group consisting of units of formulae:



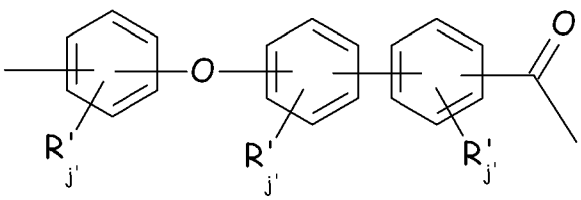
(K-A)



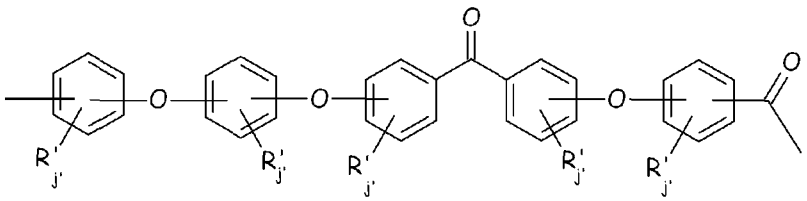
(K-B)



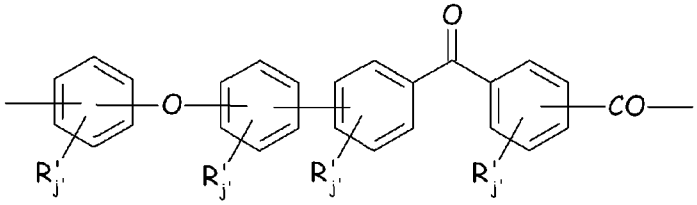
(K-C)



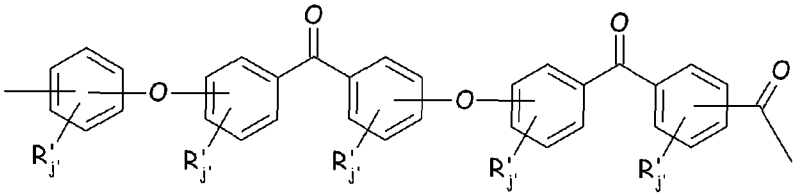
(K-D)



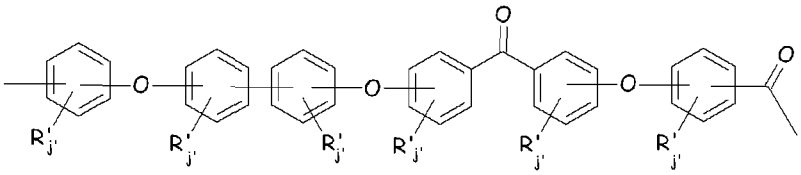
(K-E)



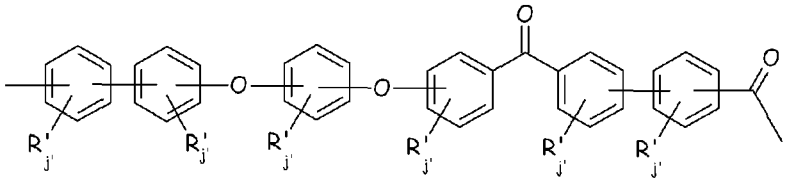
(K-F)



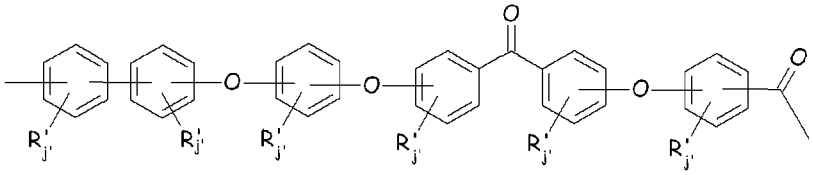
(K-G)



(K-H)



(K-I)



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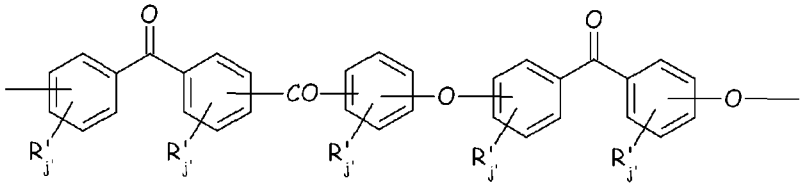
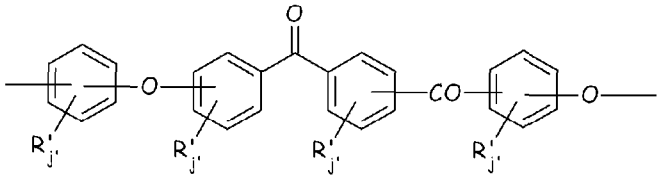


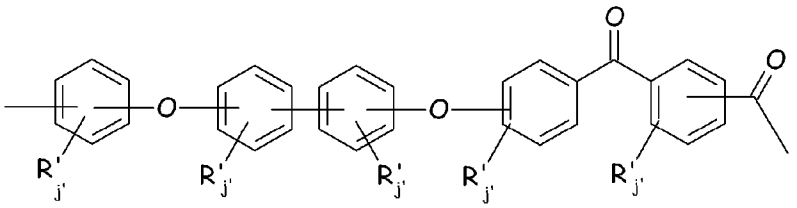
(K-K)



(K-L)

,

and



,

wherein in each of formulae (K-A) to (K-M) above:

each of R', equal to or different from each other, is independently selected at each occurrence from a C1-C12 group optionally comprising one or more than one heteroatom; sulfonic acid and sulfonate groups; phosphonic acid and phosphonate groups; amine and quaternary ammonium groups; and

each of j', equal to or different from each other, is independently selected at each occurrence from 0 and an integer of 1 to 4, preferably j' being equal to zero.

[0055] It is nevertheless generally preferred for the PEEK-PEDEK copolymer of the present invention to be essentially comprised of repeat units (RPEDEK) and (RPEEK), as above detailed. Thus, in some embodiments, the PEEK-PEDEK copolymer consists essentially of repeat units RPEDEK and RPEEK. As used herein, the expression "consists essentially of repeat units RPEDEK and RPEEK" means that any additional repeat unit different from repeat units RPEDEK and RPEEK, as above detailed, may be present in the PEEK-PEDEK copolymer in amount of at most 1 mol.%, relative to the total number of moles of repeat units in the PEEK-PEDEK copolymer, and so as not to substantially alter the advantageous properties of the PEEK-PEDEK copolymer.

[0056] Repeat units (RPEDEK) and (RPEEK) are present in the PEEK-PEDEK copolymer in a (RPEDEK)/(RPEEK) molar ratio ranging from 5/95 to 95/5, preferably 10/90 to 90/10, more preferably from 20/80 to 80/20. The "PEDEK/PEEK mole ratio" is used interchangeably herein with the "(RPEDEK)/(RPEEK) molar ratio."

[0057] According to an embodiment, the poly(ether ether ketone)-poly(ether diphenyl ether ketone) (PEEK-PEDEK) copolymer is a PEEK-rich copolymer. In that case, the (RPEDEK)/(RPEEK) molar ratio in the poly(ether ether ketone)-poly(ether diphenyl ether ketone) (PEEK-PEDEK)

copolymer, ranges from 5/95 to 50/50, for example from 10/90 to 45/55 or from 15/85 to 40/60.

[0058] According to an embodiment, the poly(ether ether ketone)-poly(ether diphenyl ether ketone) (PEEK-PEDEK) copolymer is a PEDEK-rich copolymer. In that case, the (RPEDEK)/(RPEEK) molar ratio in the poly(ether ether ketone)-poly(ether diphenyl ether ketone) (PEEK-PEDEK) copolymer, ranges from 50/50 to 95/5, for example from 60/40 to 90/10 or from 70/30 to 85/15.

[0059] The PEEK-PEDEK copolymer may exhibit a melt viscosity (MV) ranging from 0.1 to 5 kN-s/m^2, preferably 0.1 1 to 2 kN-s/m^2, more preferably 0.12 to 1.5 kN-s/m^2. measured pursuant to ASTM D3835 at 4 10 °C and a shear rate of 46 s^{-1} using a tungsten-carbide die with the following characteristics: diameter = 1.016 mm, length = 20.32 mm, cone angle = 120°.

[0060] The PEEK-PEDEK copolymer may present in the composition (C) in an amount of at most 99.5 wt.%, preferably at most 99 wt.%, 98 wt.%, 95 wt.%, 90 wt.%, 80 wt.%, based on the total weight of the composition (C).

[0061] In some embodiments, the PEEK-PEDEK copolymer is present in the composition (C) in an amount of at least 50 wt.%, preferably at least 60 wt.%, 70 wt.%, 80 wt.%, 90 wt.%, 95 wt.%, based on the total weight of the composition (C).

[0062] In some embodiments, the amount of PEEK-PEDEK copolymer in the composition (C) ranges from 50 wt.% to 99 wt.%, from 60 wt.% to 98 wt.%, from 70 wt.% to 97 wt.%, from 80 wt.% to 96 wt.% or from 90 wt.% to 95 wt.%, based on the total weight of the composition (C).

[0063] In some embodiments, the amount of PEEK-PEDEK copolymer in the composition (C) ranges from 40 wt.% to 95 wt.%, preferably from 50 wt.% to 90 wt.%, more preferably from 55 wt.% to 85 wt.%, and most preferably from 60 wt.% to 80 wt.%, based on the total weight of the composition (C).

[0064] Metallic coating

The present invention relates to an article or a part, comprising at least one coating (2) of metal having a thickness of at least 20 pm, preferably at least 30 pm, and more preferably at least 40 pm.

[0065] As used herein, the term “coating of metal”, "metallic coating" or "metallic layer" means a metallic deposit/layer applied to part of or the entire exposed surface of an article. The metallic coating is intended to adhere to the surface of the polymer substrate to provide mechanical strength, wear resistance, aesthetic appeal, anti-microbial properties and a low coefficient of friction.

[0066] The coating of metal may be fine-grained and/or coarse-grained. As used herein, the term “fine-grained” means average grain-size ranging from 2 nm to 5,000 nm. As used herein, the term “coarse-grained” means average grain-size above 5,000 nm.

[0067] The article or a part of the present invention may comprise several metallic coatings of different thicknesses and compositions. For example, it may comprise a metallic coating having a thickness of at least 20 pm and an additional coating having a thickness of less than 20 pm, for example less than 10 pm. As another example, it may comprise a coarse-grained metallic coating having a thickness of at least 40 pm and an additional fine-grained coating having a thickness of less than 20 pm, for example less than 10 pm.

[0068] The grain size can be uniform throughout the deposit; alternatively, it can consist of layers with different microstructure/grain size. Layering and/or grading the metallic layer by changing the composition, grain size or any other physical or chemical property is within the scope of this invention as well.

[0069] According to the present invention, the entire polymer surface can be coated; alternatively, metal patches or sections can be formed on selected areas only (e.g. without the need to coat the entire article).

[0070] The coating of metal is preferably be substantially porosity-free.

[0071] According to an embodiment, the coating of metal has a minimal thickness of at least 20 pm, preferably at least 30 pm, even more preferably at least 40 pm.

[0072] According to an embodiment, the coating of metal has a maximum thickness of 50 mm, preferably 40 mm, or even more preferably 30 or 20 mm.

[0073] Articles and parts of the present disclosure comprise a single or several metallic layers applied to the first layer (1) of a composition (C) as well as multi-layer laminates composed of alternating layers of metallic layers, which can for example be fine-grained and/or coarse-grained.

[0074] According to an embodiment, the composition of the metal coating comprises at least one metal selected from the group consisiting of Ag, Al, Au, Co, Cr, Cu, Fe, Ni, Mn, Mo, Pb, Pd, Pt, Rh, Ru, Sn, Ti, W, Zn, Zr and combinations thereof.

[0075] Optional components can be added to the composition of the metal coating as follows:

- metals: Ag, Al, In, Mg, Si, Sn, Pt, Ti, V, W, Zn;
- metal oxides: Ag20, AI2O3, S1O2, Sn02,Ti02, ZnO;
- carbides of B, Cr, Bi, Si, W;
- carbon: carbon nanotubes, diamond, graphite, graphite fibers);
- glass;
- glass fibers; and
- polymer materials: PTFE, PVC, PE, PP, epoxy resins.

[0076] According to a preferred embodiment, the metal is selected from the group consisting of Al and Ti.

[0077] Optional additional layers

[0078] The article or part of the present invention may comprise one or several layers: an etching layer, an anodized layer, a die coloring layer, a top layer.. . etc.

[0079] According to an embodiment, the article or part comprise an anodized layer (3) and/or a top layer (4).

[0080] Methods of making the composition (C)

[0081] Exemplary embodiments also include methods of making the composition (C).

[0082] The composition (C) can be made by methods well-known to the person of skill in the art. For example, such methods include, but are not limited to,

melt-mixing processes. Melt-mixing processes are typically carried out by heating the polymer components above the melting temperature of the thermoplastic polymers thereby forming a melt of the thermoplastic polymers. In some embodiments, the processing temperature ranges from about 280-450°C, preferably from about 290-440°C, from about 300-430°C or from about 310-420°C. Suitable melt-mixing apparatus are, for example, kneaders, Banbury mixers, single-screw extruders, and twin-screw extruders. Preferably, use is made of an extruder fitted with means for dosing all the desired components to the extruder, either to the extruder's throat or to the melt. In the process for the preparation of the layer (1), the components of the composition (C), e.g. the PAES, the PAEK, and the additional components, for example the glass fibers, are fed to the melt-mixing apparatus and melt-mixed in that apparatus. The components may be fed simultaneously as a powder mixture or granule mixer, also known as dry-blend, or may be fed separately.

[0083] The order of combining the components during melt-mixing is not particularly limited. In one embodiment, the component can be mixed in a single batch, such that the desired amounts of each component are added together and subsequently mixed. In other embodiments, a first sub-set of components can be initially mixed together and one or more of the remaining components can be added to the mixture for further mixing. For clarity, the total desired amount of each component does not have to be mixed as a single quantity. For example, for one or more of the components, a partial quantity can be initially added and mixed and, subsequently, some or all of the remainder can be added and mixed.

[0084] Methods of coating the composition (C) with a metal, methods for perapring the part/article

[0085] Another aspect of the invention is a process for preparing the article/part of the present invention, by metallisation of an article/part comprising a first layer of a composition (C) which comprises a polymeric component comprising at least one poly(ether ether ketone)-poly(ether diphenyl ether ketone) (PEEK-PEDEK) copolymer, wherein the composition (C) has a

melting temperature (Tm) of at least 290°C, as measured by differential scanning calorimetry (DSC) according to ASTM D3418.

[0086] The metallic coating can be produced by direct current DC or pulse electrodeposition, electroless deposition, physical vapor deposition (PVD), chemical vapor deposition (CVD) and gas condensation or the like.

[0087] The person skilled in the art of plating knows how to electroplate or electroless plate selected metals, alloys or metal matrix composites choosing suitable plating bath formulations and plating conditions. Similarly, the person skilled in the art of PVD, CVD and gas condensation techniques knows how to prepare metal, alloy or metal matrix composite coatings.

[0088] According to an embodiment, the metallisation is performed by physical vapor deposition (PVD) in a high vaccum environment using thermal evaporation equipment.

[0089] According to an embodiment, the article/part is heated a processing temperature (Tp) ranging from 250 to 340°C before metal deposition for example from 260 to 330°C or from 270 to 320°C.

[0090] The surface of the polymer composition (C) may be etched prior to metallization, in order to increase the roughness of the surfaces, change the surface chemical constitution, degrade or dissolve low molecular weights which migrate to the surface, and relieve residual surface stresses. The adhesion and durability of the metallic coating can notably be improved by the condition of the surface of the composition (C).

[0091] According to an embodiment, the article/part is etched (or milled) using a chemical solution before metal deposition. With the chemical etching or milling, part of the composition (C) is removed from the surface of the part/article by treatment thereof to obtain a part/article having a desired structural or ornamental configuration. The chemical etching solution may comprise sulfuric acid, for example a mixture of sulfuric acid and at least one carboxylic acid, for example phosphoric acid and/or nitric acid, as described in U.S. Pat. No. 5,160,600. Chromic acid etching solutions may also be used, as described, for example, in U.S. Pat. No. 4,610,895, U.S. Pat. No. 6,645,557 and U.S. Pat. No. 3,445,350. Permanganate

solutions (e.g. hot alkaline permanganate solution that also contains a material, such as sodium hypochlorite; alkaline permanganate solution comprising potassium permanganate and sodium hydroxide, solution that comprises water, permanganate ions, and manganate ions) may also be used, as described for example in U.S. Pat. No. 3,625,758, U.S. Pat. No. 4,042,729, U.S. Pat. No. 5,648,125, and U.S. Pat. No. 4,948,630. An electrolyte comprising manganese(lll) ions in a solution of 9 to 15 molar sulfuric acid or phosphoric acid may also be used, as described in U.S. patent application 2013/0186774 A 1.

[0092] According to an embodiment, the article/part is anodized after metal deposition. Anodizing is accomplished by immersing the mettalized part/article into an acid electrolyte bath and passing an electric current through the medium. A cathode is mounted to the inside of the anodizing tank; the metal, e.g. aluminium, acts as an anode, so that oxygen ions are released from the electrolyte to combine with the metal atoms, e.g. Al, at the surface of the part being anodized.

[0093] According to an embodiment, the article/part is polished before or after metal deposition.

[0094] According to an embodiment, the article/part is colored before or after metal deposition.

[0095] Applications

[0096] The articles and parts can be employed in a very wide variety of industrial sectors in which metallic surfaces are required, for example in the automotive industry, for instance for surrounds of display instruments, radios, door handles, and for window levers, heating grilles, dashboard buttons, headlamp reflectors, rear lights, etc., and also in the radio, TV and electronics industry, especially for printed circuits, and also in multilayer and hybrid circuits, and as chip supports, and in EMI shielding installations, etc.; they are used, moreover, in the aircraft industry, in dentistry and medicine, in the optics industry, for example in the production of mirrors, and in household articles and electrical appliances.

[0097] The articles and parts are preferably employed in electrical & electronic applications, mobile electronics, smart devices & wearables and smart phones.

[0098] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

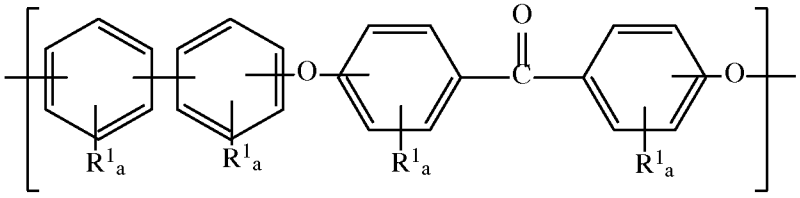
Claims

Claim 1. An article or a part, comprising:

- a first layer (1) of a composition (C) comprising at least one poly(ether ether ketone)-poly(ether diphenyl ether ketone) (PEEK-PEDEK) copolymer, wherein the composition (C) has a melting temperature (Tm) of at least 290°C, as measured by differential scanning calorimetry (DSC) according to ASTM D3418, and
- at least one coating (2) of metal having a thickness of at least 20 pm, preferably at least 30 pm, more preferably at least 40 pm.

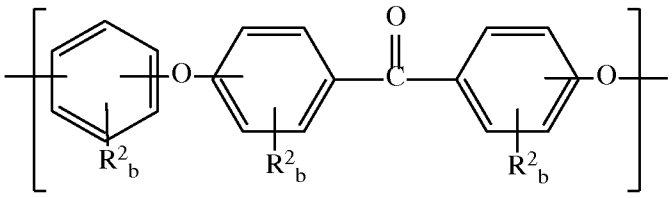
Claim 2. The article/part of any one of the preceding claims, wherein the PEDEK-PEEK copolymer comprises:

- repeat units (RPEDEK) of formula:



(A), and

- repeat units (R_{PEEK}) of formula :



(B),

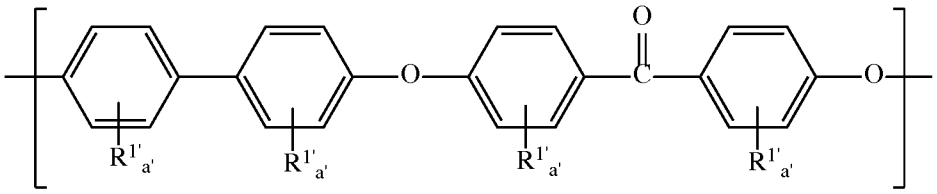
wherein:

each of R^1 and R^2, equal to or different from each other, is independently at each occurrence selected from the group consisting of halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary ammonium;

each a and b is independently selected from the group consisting of integers 0 to 4; and

the PEDEK-PEEK copolymer comprises at least 50 mol %, collectively, of the repeat units (RPEDEK) and (RPEEK), relative to the total number of moles of repeat units in the PEDEK-PEEK copolymer.

Claim 3. The article/part of any one of the preceding claims, wherein repeat units **(RPEDEK)** are repeat units of formula:



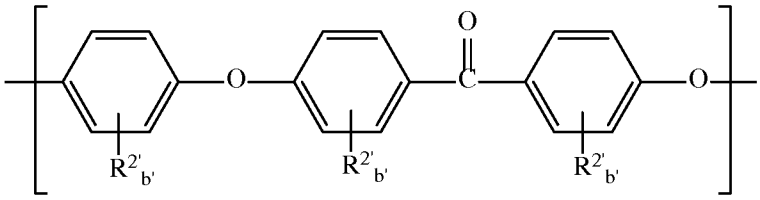
(A-1),

Wherein:

each $R^{1'}$, equal to or different from each other, is independently at each occurrence selected from the group consisting of halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary ammonium; and

a' is independently selected from the group consisting of integers 0 to 4.

Claim 4. The article/part of any one of the preceding claims, wherein repeat units **(RPEEK)** are repeat units of formula:



(B-1),

wherein:

each $R^{2'}$, equal to or different from each other, is independently at each occurrence selected from the group consisting of halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary ammonium; and

b' is independently selected from the group consisting of integers 0 to 4.

Claim 5. The article/part of any one of the preceding claims, wherein the composition (C) comprises from 50 wt.% to 99 wt.% of at least one PEDEK-PEEK copolymer, based on the total weight of the polymer composition.

Claim 6. The article/part of any one of the preceding claims, wherein the composition (C) also comprises glass fibers and/or carbon fibers.

Claim 7. The article/part of any one of the preceding claims, wherein the metal is selected from the group consisting of Al and Ti.

Claim 8. The article/part of any one of the preceding claims, further comprising an anodized layer (3) and/or a top layer (4).

Claim 9. Process for preparing the article/part of any one of claims 1-8, by metallisation of an article/part comprising a first layer of a composition (C) which comprises a polymeric component comprising at least one poly(ether ether ketone)-poly(ether diphenyl ether ketone) (PEEK-PEDEK) copolymer, wherein the composition (C) has a melting temperature (Tm) of at least 290°C, as measured by differential scanning calorimetry (DSC) according to ASTM D3418.

Claim 10. The process of claim 7, wherein the metallisation is performed by physical vapor deposition (PVD) in a high vaccum environment using thermal evaporation equipment.

Claim 11. The process of claim 7 or 8, wherein the article/part is heated a processing temperature (Tp) ranging from 250 to 340°C before metal deposition.

Claim 12. The process of any one of claims 7-9, wherein the article/part is etched using a chemical solution before metal deposition.

Claim 13. The process of any one of claims 7-10, wherein the article/part is polished before or after metal deposition.

Claim 14. The process of any one of claims 7-11, wherein the article/part is:
- colored before or after metal deposition, and/or
- anodized after metal deposition.

Claim 15. Use of the article/part of any one of claims 1-6, for electrical & electronic applications, mobile electronics, smart devices & wearables and smart phones.

INTERNATIONAL SEARCH REPORT

International application No
PCT/ EP20 19/068462

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L71/10 C23C14/20 C08G65/40 C09D171/00
ADD.

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)
C23C C09D C08L C08G C09J

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 practicable, 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	WO 2018/024744 A1 (SOLVAY SPECIALTY POLYMERS USA [US]) 8 February 2018 (2018-02-08) examples E1-E11 page 17, lines 14-16	1-15
A	US 2014/255722 A1 (NAGARAJAN NANDAKUMAR [CA] ET AL) 11 September 2014 (2014-09-11) example 3	9-15

☐ 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) orwhich is cited to establish the publication date of another 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	Date of mailing of the international search report
30 July 2019	06/08/2019

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Scheunemann, Sven

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2019/068462

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2018024744 A1	08-02-2018	NONE	
US 2014255722 A1	11-09-2014	NONE	