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(54) **Coated plastic part and method of producing a coated plastic part**

(57) A method of producing a coated plastic part, the method comprising the steps of: forming a composite of a thermoplastic polymer and graphene or nanographene wherein the ratio of polymer and nanographene is chosen in such a way that the composite has electric conductivity; processing the composite in an extruder to produce master-batch in solid form; processing the master-batch to mold a plastic part; and applying a coating directly onto the plastic part by an electrostatic coating process.

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Description

Field of the Invention

[0001] The invention relates to a coated plastic part and a method of producing a coated plastic part wherein the part is intended to be used e.g. in automotive or other industrial equipment, such as a bumper or spoiler of a vehicle or a housing or cover of technical equipment.

Background of the Invention

[0002] In the automotive industry, it is known to form parts of the vehicle body as well as attached parts, such as car wings, bumpers and spoilers, using plastic substrates which are finished by a wet or powder coating process. Plastic parts are advantageous in that they are light weight and do not corrode. Both plastic and metal car body parts are usually coated by a wear-resistant lacquer layer which protect the car body against corrosion and other external influences, such as patrol, acids, mechanical impacts of rocks and the like. The lacquer layer further improves the outer appearance of vehicles. Coated plastic parts, of course, are also known from other industrial applications, such as housings and covers for any type of technical equipment.

[0003] In the automotive industry, it is common to apply the lacquer coating by an electrostatic wet or powder coating process. When metal parts are used, due to their inherent electric conductivity of the metal parts, the lacquer can be applied directly onto the respective metal parts. This, however, is not possible when parts are made from plastic material. For electrostatically coating plastic parts, it has been known to first coat the plastic part using a primer having sufficient electric conductivity so that a lacquer layer can be applied in a subsequent electrostatic wet or powder coating process. This requires an additional processing step. Often, a clear finish coat is applied onto the color lacquer. All of this is well known in the art.

[0004] An example of a coated article made of polypropylene using a conductive primer and an electrostatic coating process is described in EP 0 576 031 A1.

[0005] From WO 2010/072592 A1, it is also known to manufacture plastic materials and products for articles in the automotive industry having improved scratch resistance, e.g. for the interior of automobiles, by using a combination of a grafted polymer, such as grafted polyolefine, and a friction reducing agent. These materials are intended to be used without any coating. Besides the automotive industry, the materials are also indicated to be useful in other fields, e.g. for machine housings, appliances, consumer electronic devices.

[0006] DE 198 54 238 B4 describes a composition comprising carbon black and a polymer of the formula $H-[X-R^1-X-CO-Y-CO]_n-OH$ for forming a powder coated part. The composition is electrically conductive so that it is possible to apply powder by an electrostatic coating process. The coated part can be used as a housing, car body part or the like.

[0007] EP 0 667 625 describes an electrostatic coated polymer material, including carbon fibers and a metallic powder.

[0008] WO 2006/025555 A1 describes electrically conductive composites made from a polymer including carbon-based conductive fillers such as carbon black and carbon nanotubes. The parts are finished by an electrostatic coating process.

[0009] WO 2008/019185 A1 describes a thermoplastic article including a blend of poly(arylen ether) and polyamide, an electrically conductive carbon black, and an impact modifier. The article is coated using an electrostatic powder or wet coating process.

[0010] WO 2010/102731 A1 describes a form part including a mixture of a thermoplastic polymer and carbon nanotubes for achieving high surface electric conductivity. Also single or multi-layer graphite structures in the form of graphene can be used. The part is used in antistatic or electrically conductive housings for household or electric devices or for components of vehicles which need to have high surface conductivity.

[0011] There is a large number of further documents disclosing antistatic or electrically conductive polymers including graphite and methods of their production, including the functionalisation of graphite and graphenes, such as DE 10 2008 038 524 A1; WO 2008/097343 A2; US 2011/0017587 A1; EP 2 216 358 A1; EP 2 266 786 A1; US 7,923,491 B2; US 2010/0247892 A1; WO 2009/123771 A2; WO 2009/134492 A2; WO 2009/147415 A1; WO 2010/072592 A1; WO 2010/086176 A1.

[0012] It is an object of the present invention to provide a coated plastic part and a method of its manufacture which can be realized with low expense and exhibits a high quality surface finish.

Summary of the Invention

[0013] This object is solved by a method of producing a coated plastic part according to claim 1 and by a coated plastic part according to claim 14. Preferred embodiments of the invention are defined in the dependent claims.

[0014] The method of the present invention comprises the steps of Forming a composite of a thermoplastic polymer and graphene or nanographene wherein the ratio of polymer and graphene and/or nanographene is chosen in such a way that the composite has low electric resistance. More particularly, the electric conductivity shall be high enough to allow an electrostatic coating process, more particularly an electrostatic wet painting process. The composite is processed in an extruder to produce master-batch pellets or powder and these are processed to mold a plastic part, for example by injection molding or extrusion. The latter step, as such, is performed in a manner well known in the art wherein the master-batch pellets and standard polymer or copolymer

pellets are mixed and then homogenized and molten in an injection molding tool, for example, to form the final product. Onto the prefabricated plastic part, a coating is applied directly by an electrostatic coating process, that is without the intermediary of an electrically conductive primer or other intermediary which would support adhesion of the lacquer on the prefabricated plastic part.

[0015] In the context of the present invention, the term "pellets" refers to any particles of processed polymer or polymer composite suitable for use e,g. in an injection molding or extrusion process, without being limited to any particular size or shape of particles. The use of the term "pellets" does not exclude any suitable other form of polymer, such as powder, but shall designate any suitable master-batch in solid form.

[0016] While it has been known in the prior art, as discussed above, to form electrically conductive plastic parts by incorporating graphite into a polymer material, the largest part of the prior art considers the use of carbon black or carbon nanotubes rather than graphene or nanographene which is distinct from the graphite structures most commonly used in the prior art applications. Graphene is a flat mono layer of carbon atoms tightly packed in a two-dimensional chrystallographic latice. The use of graphene sheets has been proven to be superior over the previously more commonly used carbon black, carbon fibers and carbon nano-tubes in that it has an extremely high Young modulus of about 1000 Gpa, high electric conductivity in the plane of the graphene sheets of more than 20000 S/cm, high thermal conductivity of more than 5300 W/mK, and an extremely high surface area of approximately 2675 m^2/g. Moreover, graphene sheets are easy to functionalize and can disperse in many thermoplastics, resins and solvents. Graphene hence is an ideal supplement for imparting electric conductivity to a plastic part which, in addition, can be manufactured at relatively low costs. A composite of a thermoplastic polymer and graphene or nanographene is hence an ideal raw material for producing plastic parts which are to be coated by an electrostatic coating process, in particular electrostatic wet lacquering, for large-scale production.

[0017] In a preferred embodiment, the thermoplastic polymer for forming the master-batch pellets as well as the polymer or copolymer pellets added in the molding process comprises at least one of a polystyrene, such as acrylonitrile butadiene styrene or acrylester styrol acrylnitril; one of a polyolefin, such as polypropylene or polyethylene; a polyester; or a blend of any of these materials.

[0018] Preferably, the graphene or nanographene is functionalized, for example by attaching chemical bonds and/or by chemical interaction and the composite is prepared in self-assembled monolayers (SAM).

[0019] In the preferred embodiment of the invention, the graphene or nanographene comprises layers having an extension of about 200 nm to 30 μm and a thickness of about 0,3 nm to about 20 nm. In the conditioned composite, the graphene sheets can be broken into smaller parts, warped, folded and/or deformed similar to a very fine piece of gauze.

[0020] In the preferred embodiment of the invention, the plastic part is formed by injection molding or extrusion and coated by a wet coating process.

[0021] For forming the composite, single-layer graphene and/or multi-layer graphene can be used wherein the polymer and graphene or nanographene are mixed by an extrusion process. In the preferred embodiment of the invention, the composite does not include any carbon nanotubes and/or carbon nanofibers and/or carbon fibers and/or carbon black but carbon is present in the composite only in the form of graphene or nanographene.

[0022] In one embodiment of the invention, the ratio of polymer and graphene or nanographene is chosen in such a way that the composite of the master-batch and/or pellets or the plastic part has an electric resistivity in the range of 1 MΩ/cm to 10 kΩ/cm. More particularly, the ratio of polymer and graphene or nanographene can be chosen such that graphene is present in an amount of about 0.1 to 25 wt.% in the master-batch pellets or in the final product. A compatibilizer, such as maleic anhydride or aminopropyl silane or stearic acid, can be added to the graphene or nanographene to support blending the graphene sheets into the polymer.

[0023] The present invention also provides a coated plastic part which comprises an electrically conductive plastic base substrate, the plastic substrate being made from a composite of a thermoplastic polymer and graphene or nanographene, and a coating composition directly apply to the plastic substrate by an electrostatic coating process without the intermediary of an electrically conductive primer. The coated plastic part can have anyone of the properties discussed above in the context of the method of the present invention or any combination of properties discussed above.

[0024] In a preferred embodiment, the coated plastic part is a part of a vehicle or a part of another manufactured equipment, such as a bumper, a spoiler, a housing, or a cover.

Brief Description of Drawings

[0025]

Fig. 1 shows a flow diagram of a method of producing a coated plastic part according to the invention;

Fig. 2 shows an overview of a production line for performing the process of the present invention;

Fig. 3 shows a schematic diagram of an extruder for producing pellets to be used in the process of the present invention;

Fig. 4 schematically show an example of functionalized graphene to be used in the process of the present invention; and

Fig. 5A and 5B show microscopic photographs af graphene sheets for use in the present invention.

Description of Embodiments

[0026] The process according to a preferred embodiment of the invention is schematically shown in the flow diagram of Fig. 1. The raw materials for manufacturing the coated plastic part of the present invention are graphene or nanographene and a thermoplastic polymer. In the example of Fig. 1, the process comprises the steps of preparing functionized nanographene 10 and a polypropylene (PP) base material 20. The materials are mixed in an extruder 30 to form a master batch granulate 32 at the extruder exit. The extruder preferably is a twin screw or planetary extruder which thoroughly mixes and kneads the composite wherein the graphene sheets can be broken, bend, warped and, more generally, deformed so as to intimately mix with the polymer.

[0027] The masterbatch granulate or pellets and/or powder containing graphene or nanographene are introduced together with standard polymer or copolymer pellets 35 into an injection molding equipment where a plastic part is formed by injection molding 34. The molded plastic part has an electric conductivity sufficiently high to be directly coated in an electrostatic coated process. The ratio of polymer and graphene or nanographene is hence chosen in such a way that the composite or plastic part preferably has an electric resistivity in the range of 1 MΩ/cm to 10 kΩ/cm. For example, graphene or nanographene can be added to the polymer in an overall amount of 0.1 to 25 wt.-%, preferably 0,5 to 8 wt.-%, depending on the particular polymer material and optional further additives chosen. The above ratio is related to the to the overall quantity of polymer in the final products.

[0028] The injection molded part is removed from the mold and undergoes a cleaning process 36 as well as a deionization process 38. The cleaned and deionizated plastic part is then introduced into an electrostatic coating system where a base coat is applied by electrostatic painting, preferably electrostatic wet coating 40 using a liquid coating material which is applied directly onto the plastic part.

[0029] When the coating step 40 is completed, the coated part undergoes polymerization 42, and in a next step 44, an optional clear coating is applied to the plastic part, followed by a further optional step 46 of polymerization. The coated plastic part is then completed. The polymerization serves to "cure" the wet lacquer so that it becomes solid.

[0030] When compared to the process of the prior art, the use of a composite of thermoplastic polymer and graphene allows to omit additional processing steps of flaming and applying an electrically conductive primer to the pre-fabricated plastic part by an aerographic coating process, such as spray coating, so as to allow electrostatic coating of the plastic part.

[0031] Fig. 2 shows an example of equipment for manufacturing the coated plastic part according to the invention. For forming the composite, the process uses functionalized nanographene 50 or graphene and a polymer granulate 52, such as polystyrene, a polyolefin, a polyester, as raw material which are introduced into a twin screw extruder 54 to produce master-batch pellets or powder 56 from the composite. The pellets or powder 56 are then introduced into an injection molding equipment 58 where they are molded together with the standard polymer or copolymer pellets (not shown) to form a pre-fabricated plastic part 60, using a process which, as such, is known in the art. The ratio of nanographene 50 or graphene and the polymer granulate 52 is chosen in such a way that the pre-fabricated plastic part 60 has sufficient conductivity to be directly coatable in an electrostatic coating process. The electric resistivity of the composite of polymer and graphene/nano graphene or the plastic part preferably is in the range of 1 MΩ/cm to 10 kn/cm.

[0032] The pre-fabricated plastic part 60 is introduced into an electrostatic coating equipment (not shown) where wet lacquer is directly applied onto the part by electrostatic coating. Optionally, also a clear coating can be applied onto the coated plastic part.

[0033] Fig. 3 schematically shows the screw extruder 54 of Fig. 2, for forming the master-batch pellets or powder of the nanographene/polymer composite. The extruder 54 comprises a main feeder 62 for introducing the polymer and graphene/nanographene which optionally can be compatibilized with some chemical products, such as maleic anhydride or aminopropyl silane or stearic acid. These materials are conveyed and preheated in a first stage 64 of the screw extruder 54 so that the polymer is melted and pre-mixing takes place. A second stage 66 of the twin screw extruder 54 comprises a side feeder 68 where the graphene/nanographene can be added which, however, can be introduced additionally using the main feeder 62. This is designated as "filler" introduction in Fig. 3. The composition of the polymer, graphene or nanographene, optionally compatibilized, is mixed in the second stage 66 as well as in a third stage 70 and a fourth stage 72 of the screw extruder 54. The third stage 70 comprises a vent opening 74 to the atmosphere and the fourth stage 72 comprises a vacuum vent 76 for venting and degasing the mixture. At its exit, the screw extruder 54 comprises a metering zone 78 for metering the composite material to produce the master-batch pellets, or powder, or granulate to be used in the subsequent injection molding process.

[0034] Fig. 4 shows a microscopic photograph of a graphene sheet structure which can be used in the process of the present invention. It can be recognized, that the structures are tissue like.

[0035] Fig. 5A and 5B show examples of functionalized graphene and nanographene sheets respectively including bonds of additional functional groups, such as OH, EPOXI, COOH, isocyanat, amid, and carbamid. Other materials can be used for functionalizing the graphene sheets, such as silane compounds, phosphonate compounds, sulphur compounds, and organic acid compounds, for example.

[0036] As explained above, the coated plastic part according to the present invention can be used in the automotive industry as well in many other industrial applications, such as for bumpers, spoilers, housings, covers and the like.

Claims

1. A method of producing a coated plastic part, the method comprising the steps of:

   forming a composite of a thermoplastic polymer (52) and graphene or nanographene (50) wherein the ratio of polymer and nanographene is chosen in such a way that the composite has electric conductivity;
   processing the composite in an extruder (54) to produce masterbatch pellets or powder (56);
   processing the masterbatch pellets or powder (56) together with standard polymer or copolymer pellets to mold a plastic part (60); and
   applying a coating directly onto the plastic part (60) by an electrostatic coating process.

2. The method of claim 1 wherein at least one of the thermoplastic polymer (52) for forming the master batch pellets or powder and the standard polymer or copolymer pellets added to the master-batch pellets or powder are selected from the group consisting of: a polystyrene, such as acrylonitrile butadiene styrene or acrylester styrol acrylnitril; one of a polyolefin, such as polypropylene or polyethylene; a polyester; or a blend of any of these materials.

3. The method of one of the preceding claims wherein the graphene or nanographene is functionalized.

4. The method of one of claim 3 wherein the graphene or nanographene is functionalized by chemical bonds and/or chemical interaction and finally prepared in self assembled monolayers, SAM.

5. The method of one of the preceding claims wherein the graphene or nanographene comprises layers having an extension of about 200 nm to 30 μm and a thickness of about 0.3 nm to about 20 nm.

6. The method of one of the preceding claims wherein the plastic part (60) is formed by injection molding or extrusion.

7. The method of one of the preceding claims wherein the electrostatic coating process is a wet coating process.

8. The method of one of the preceding claims wherein single-layer graphene and/or multi-layer graphene is used form forming said composite.

9. The method of one of the preceding claims wherein the ratio of polymer and graphene or nanographene is chosen in such a way that the composite or the plastic part has an electric resistivity in the range of 1 MΩ/cm to 10 kΩ/cm.

10. The method of one of the preceding claims wherein the ratio of polymer and graphene or nanographene is chosen such that nanographene is present in an amount of 0,1 to 25 wt.-%.

11. The method of claim 10 wherein the polymer and graphene or nanographene are mixed by extrusion processing.

12. The method of one of the preceding claims wherein a compatibilizer, such as maleic anhydride or g-aminopropyl silane or stearic acid is added to the graphene or nanographene.

13. The method of one of the preceding claims wherein the composite does not include any carbon nanotubes and/or carbon nanofibres and/or carbon fibres and/or carbon black.

14. A coated plastic part, comprising:

   an electrically conductive plastic base substrate, the plastic substrate made from a composite of a thermoplastic polymer and graphene or nanographene; and
   a coating composition directly applied to the plastic substrate by an electrostatic coating process without the intermediary of an electrically conductive primer.

15. The coated plastic part of claim 14 which is a part of a vehicle or a part of another manufactured equipment, such as a bumper, a spoiler, a housing or a cover.

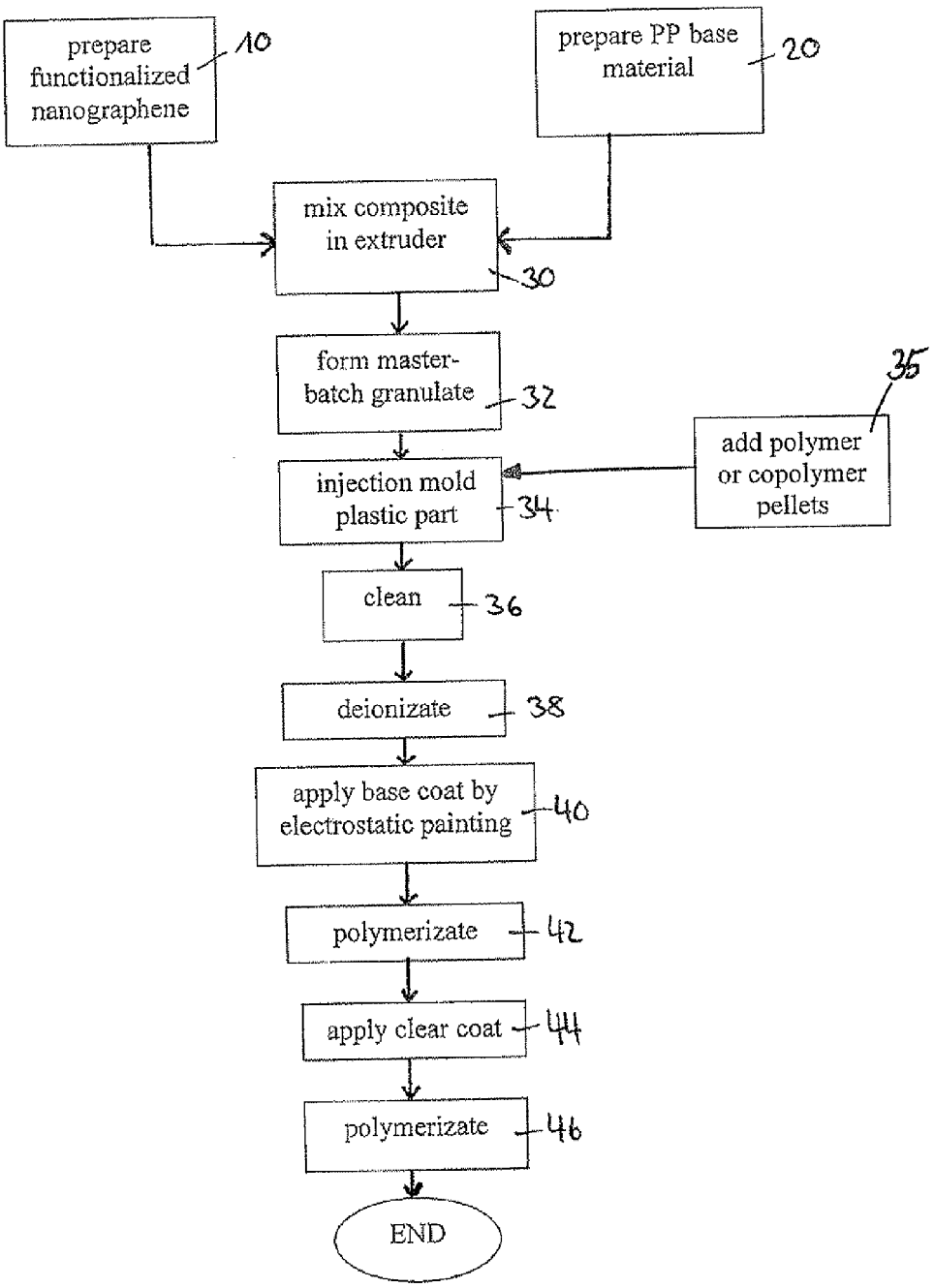

prepare functionalized nanographene
10
prepare PP base material
20
mix composite in extruder
30
form master-batch granulate
32
add polymer or copolymer pellets
35
injection mold plastic part
34
clean
36
deionizate
38
apply base coat by electrostatic painting
40
polymerizate
42
apply clear coat
44
polymerizate
46
END

Fig. 1

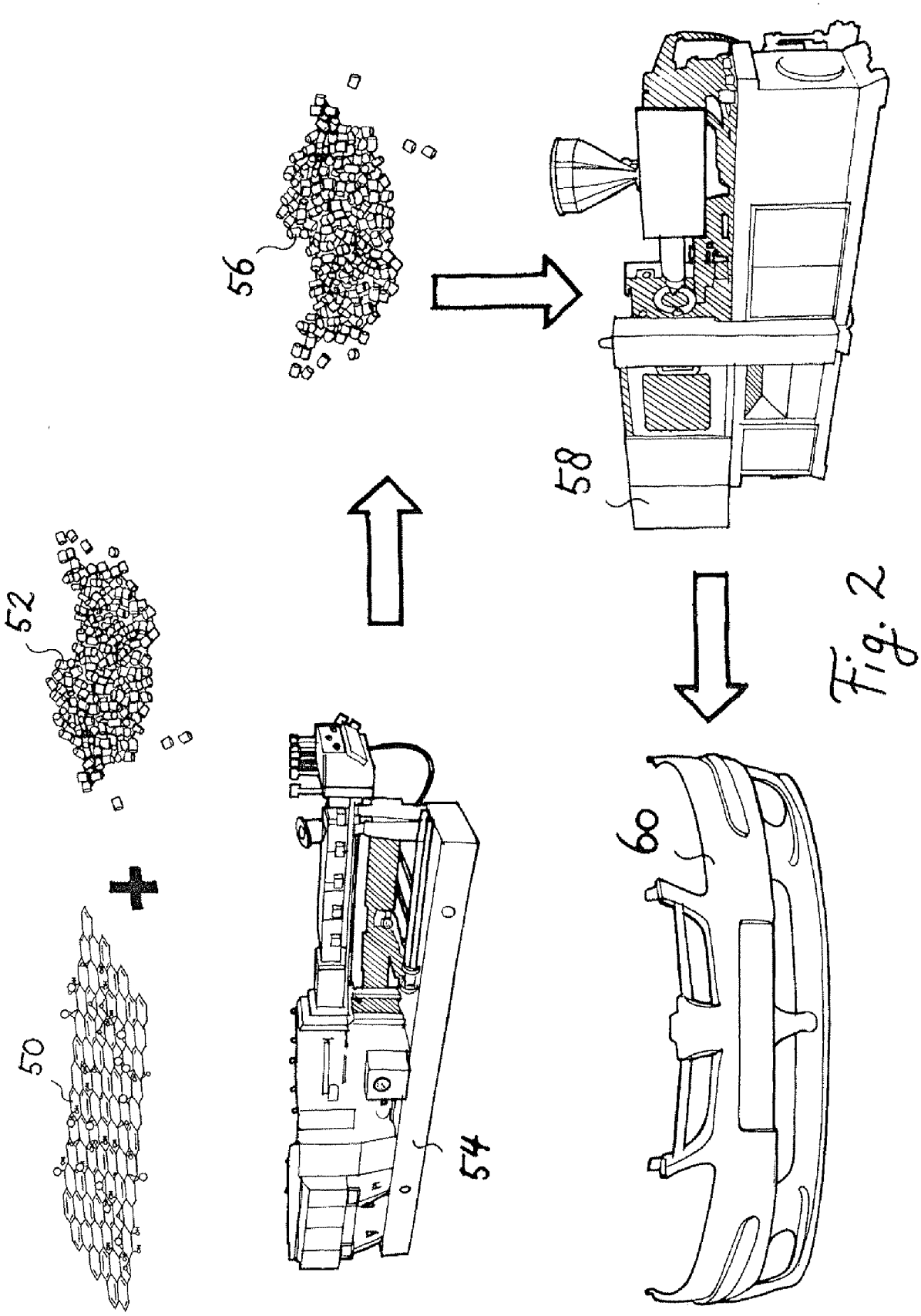


Fig. 2

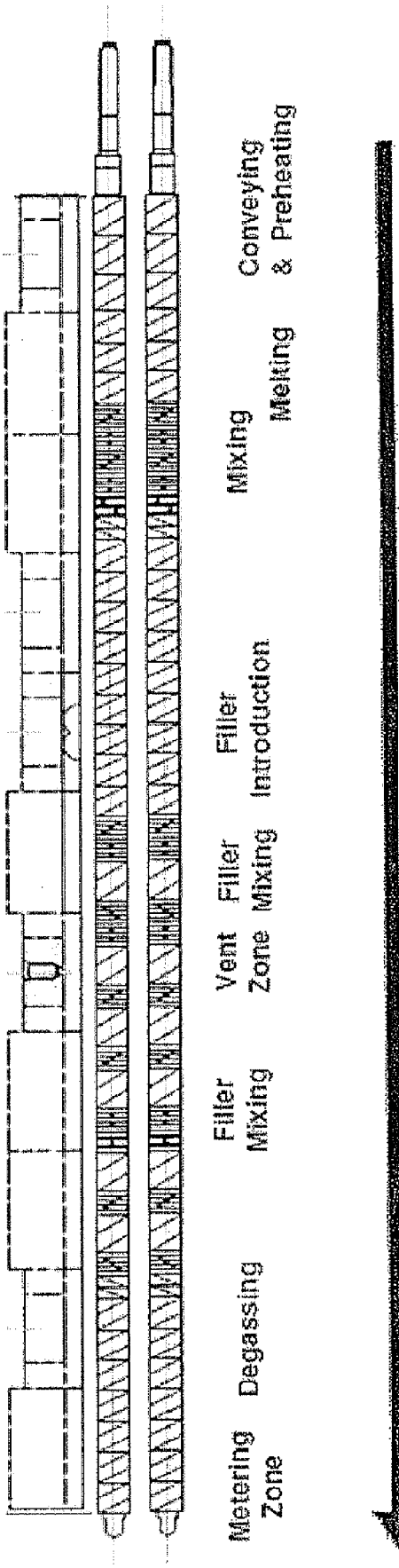
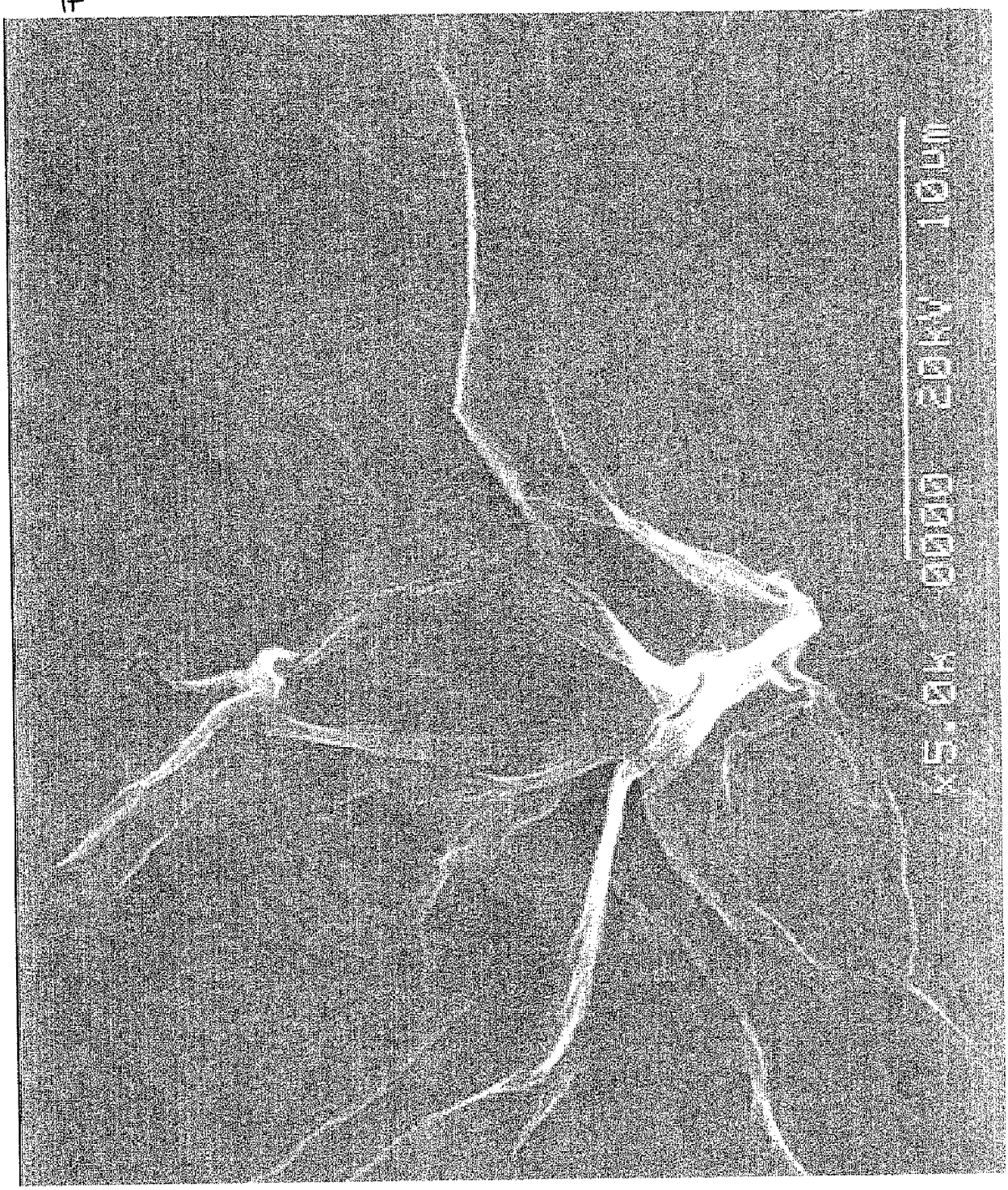

Metering Zone
Degassing
Filler Mixing
Vent Zone
Filler Mixing
Filler Introduction
Mixing
Melting
Conveying & Preheating

Fig. 3

Fig.4



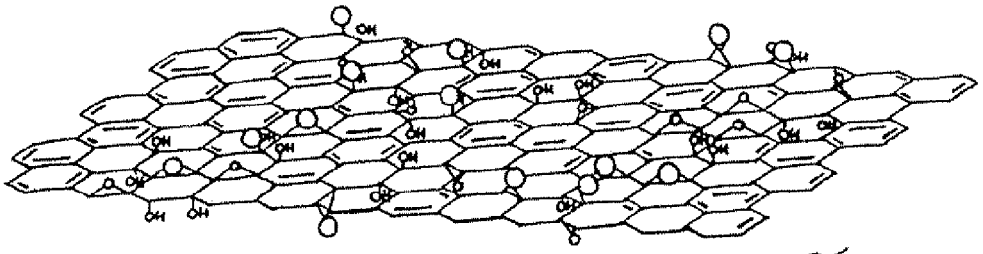
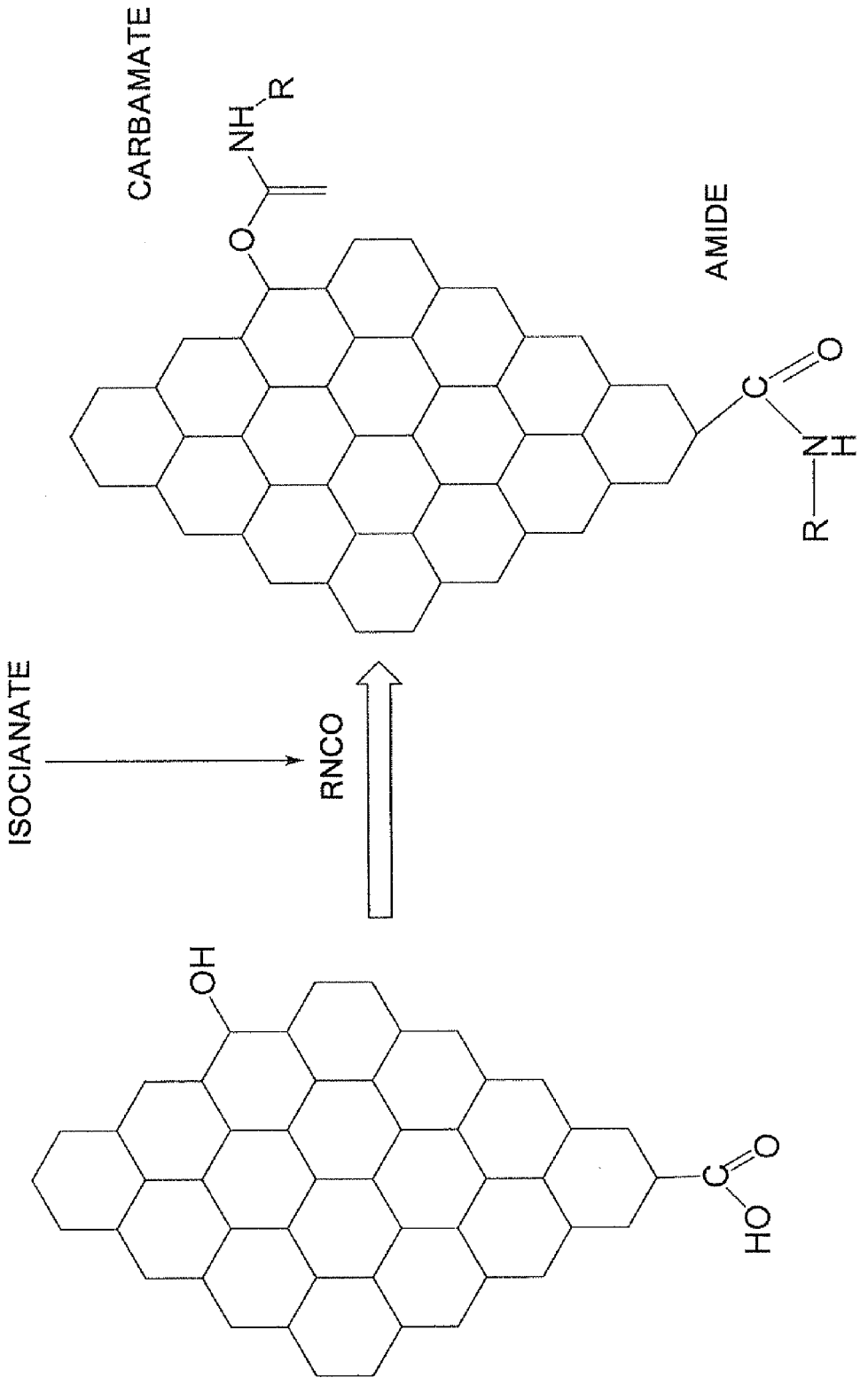


Fig. 5A

Fig. 5B



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EUROPEAN SEARCH REPORT

Application Number
EP 11 17 5089

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 2008/130431 A2 (UNIV PRINCETON [US]; PRUD HOMME ROBERT K [US]; O'NEIL CHRISTOPHER D [U) 30 October 2008 (2008-10-30) * page 3, line 22 - line 23 * * page 12, line 32 - page 13, line 4 * * page 21, line 26 - page 22, line 28 *	1-3, 5-12,14, 15	INV. B05D1/04 B05D7/02
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TECHNICAL FIELDS SEARCHED (IPC)

B05D
B29C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	22 December 2011	Slembrouck, Igor

CATEGORY OF CITED DOCUMENTS

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