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10 Electrically conductive filler and process for the production thereof

Description

15 The invention concerns an electrically conductive filler for a
conductive plastic material as set forth in the classifying portion of claim 1
and a process for the production thereof.

20 Silicone-based electrically conductive sealing materials with
conductive filling for the production of housing seals or gaskets with an
electromagnetic screening action on the spot ("mold-in-place gaskets" =
MIPG or "form-in-place gaskets" = FIPG) are known.

25 Up to the beginning of the Nineties they were used in particular for
adhesively sealing off individual parts of screening housings or for gluing
on prefabricated screening seals or gaskets during housing assembly, and
they were correspondingly adjusted in terms of their properties. In regard
to corresponding products attention is directed to data sheet CS-723
"Conductive Caulking Systems" (1972) from Tecknit, USA, Technical
Bulletin 46 "CHO-BOND 1038" (1987) from Comerics, USA, and DE-A-39
36 534.

30 DE-A-39 34 845 discloses a multi-part screening seal or gasket
which comprises an elastic carrier and a highly conductive cover layer, and
permits both prefabrication of housing parts with a seal or gasket prior to
assembly and also repeated opening of the housing after it has been
closed for the first time. This structure is intended specifically to counter
the problems of non-homogeneity, which occur by virtue of the high

density of the metal particles which afford the conductivity of the material. Production of the multi-component seal or gasket however is expensive.

Therefore, the process described in EP-B-0 629 114 has gained general acceptance in mass production, wherein the conductive material in an initial pasty condition is applied by means of pressure from a needle or nozzle directly onto a housing portion and elastically sets thereon, adhering to the surface thereof, in such a way that a shielding profile member which is at the same time conductive and elastic is formed (free from shaping structure). The configuration of the shielding profile member is predetermined by way of a suitable selection of the cross-sectional shape and size and the sweep speed of the needle or nozzle, and also by adjustment of the material properties such as viscosity, thixotropy and hardening or cross-linking rate.

In the case of known, highly conductive sealing materials, the filler materials used are in particular massive noble metal particles, for example of silver, noble metal-coated particles with a base core such as for example Ag- or Pt-coated Cu- or Ni-particles, composites of base metals such as for example Ni-coated Cu-particles, or noble metal-coated glass or ceramic particles. The carbon-based fillers which are also known cannot meet present-day requirements in terms of their conductivity.

In the course of the progressive large-scale use and falling prices of electronic equipment which only operate reliably with highly effective screening, the production of screening housings is subject to a high level of cost pressure which inter alia forces a search for inexpensive fillers which are easy to process and which are intended to permit the production of sealing materials which are variably adjustable in terms of their properties.

Therefore the object of the present invention is to provide an improved electrically conductive filler for plastic materials and a process for the production thereof.

That object is attained by a filler having the features recited in claim 1 and a process having the features of claim 10 or claim 12.

The invention includes the fundamental notion of forming the filler from gas-filled micro-hollow bodies of low density, which have an
5 elastically deformable metal casing.

The wall of the micro-hollow body is preferably of a dual-layer nature, with an inner casing comprising plastic material and is substantially gas-tight, which together affords the desired high degree of elasticity, in particular elastic compressibility, of the filler bodies. As an
10 alternative to the structure with a plastic inner casing, the wall however may also exclusively consist of a substantially closed metal layer.

A thermoplastic or thermosetting material which is filled with such a pourable filler material - more especially a conductive sealing material or a conductive gap-filling adhesive or a conductive coating material - , with a
15 volume conductivity which can be adapted to all demands, has a relatively low metal content, a low density and a high level of elasticity and resiliency and is therefore excellently well suited for many tasks in the area of electromagnetic screening but also others.

The micro-hollow bodies are advantageously of a diameter in the
20 range of between 5 μm and 100 μm , in particular between 15 μm and 50 μm , and in the simplest case have an air filling under approximately normal or atmospheric pressure. However, depending on the respective production processes involved, there may also be another filling gas, for example nitrogen or carbon dioxide. The internal pressure as a parameter
25 which substantially influences elasticity may also differ from normal pressure, in particular it may be a moderately increased pressure.

At the present moment in time, the hollow bodies can be most simply produced in approximately hollow sphere form. Adding a filler to that hollow body form (after metal coating) to give a matrix material
30 affords a seal or gasket material having isotropic mechanical and electrical properties.

In contrast, a filler in which at least a part of the micro-hollow bodies is of an approximately ellipsoidal, cylindrical or prismatic configuration (that also includes a briquette-like configuration or flake form), wherein the length of the longest major axis of an ellipsoid is at least 1.5 times the next larger major axis or the height of the cylinder is at least 1.5 times the radius or the height of the prism is at least 1.5 times the length of its largest base surface side, permits the production of a mechanically and electrically anisotropic sealing and screening material. Specifically when such a material is discharged from a needle or nozzle or when the material is applied by means of a doctor or squeegee, more specifically, due to the dynamic interface orientation effects, orientational alignment of the elongate micro-hollow bodies can occur, and subsequent hardening on the substrate preserves that orientation.

The metal casing (metal layer) preferably embraces the entire surface area of the micro-hollow bodies. It thus ensures the gas-tight integrity thereof and makes them substantially incompressible without substantially adversely affecting elasticity in respect of shape. It is of a mean thickness in the range of between 0.1 μm and 5 μm , which is so matched to the dimensions of the micro-hollow bodies that the effective density of the coated micro-hollow bodies is of the order of magnitude of the density of a plastic matrix in which the conductive filler is to be used.

The selection of the size of the micro-hollow bodies and the mean casing thickness, which is matched to each other in that way to implement a desired mean density, is effected generally with the overall aim of achieving a predetermined level of volume conductivity. It is to be observed in this respect that the conductivity of the filler in a matrix is moreover also substantially influenced by the structure of the coating (see hereinafter).

Particularly high material cost savings are possible in an embodiment in which the metal casing comprises at least two layers, wherein only the outer layer is a noble metal layer.

The surface of the metal coating is preferably rough or porous, down to heavily structured coatings with crystallite-like or dendritic or stellate, substantially radially oriented extensions from the coating material, which ensure an intimate connection to the matrix in a sealing material and - by way of methodical interlocking of the hollow bodies which are adjacent to each other in the matrix - a high level of volume conductivity, even with a relatively low degree of filling.

A pronounced surface structure of that kind is advantageously formed by vacuum coating processes, for example vapor deposit in vacuum, or in a sputtering process.

The conductive coating is inexpensively formed preferably by means of a current-less and/or electrolytic liquid phase metallization process or galvanization process. In that respect, the procedure for forming the conductive coating - in particular on micro-hollow bodies comprising plastic material - desirably includes a first step of forming a first metallization layer in a current-less metallization process and a second step of forming a second metallization layer in an electrolytic metallization process.

As an alternative to coating in a metallization bath, the conductive coating is formed by means of a gaseous phase metallization process, in particular vacuum vapor deposit or reactive sputtering.

Particularly in the liquid phase variant, the procedure preferably involves, before or after the formation of the conductive coating, at least one step of superficial cauterizing or etching of the surface of the micro-hollow bodies in order to roughen up the surface or render it porous. Such a treatment prior to the metallization operation improves the adhesion of the metal layer or in the case of certain thermoplastic materials first ensures that they do in fact enjoy sufficient adhesion.

Advantageous developments of the invention are also characterized in the appendant claims and are set forth in greater detail hereinafter in the context of the description of preferred embodiments of the invention.

In a first embodiment the filler comprises plastic hollow spheres (for example of PVDC = polyvinylidene chloride, PTFE = polytetrafluoroethylene, acrylonitrile or polypropylene) of a mean diameter of about 20 μm with an Ag-coating which is heavily crystal-like structured, of a mean thickness (estimated from weight or density) of between about 300 nm and 1 μm , which was precipitated from the gaseous phase onto the hollow spheres accommodated in a special bulk material sample holder. The pronounced surface structure can be achieved by suitable adjustment of the process parameters, for example HF-voltage, temperature of the sample holder and material and carrier gas composition and flow rates in a sputtering process, without the need for a special preliminary or subsequent treatment.

However, in a modification of the first embodiment, surface etching of the initial hollow spheres in a per se known chromosulfuric acid or alkali hydroxide etching bath makes it possible to produce a primary structure in the plastic surface, on which there is then advantageously superimposed a secondary structure of the Ag-layer, produced by suitable process implementation in the coating step, so that - relative to the mean particle diameter - large peak-to-peak spacings can be achieved. A filler of that kind affords synthetic resin-based sealing material a sufficiently high level of conductivity, even at a relatively low level of concentration, and in addition has a particularly low tendency to sedimentation.

In a second embodiment the filler comprises approximately cuboidal thermoplastic hollow bodies (for example one of the above-mentioned polymers and/or polyimide) with "edge" lengths in the range of between 10 and 40 μm and a metallization comprising an Ni-layer and thereover a porous Ag-layer of a total thickness of about 2 μm . The operation of applying the Ni-layer is effected after etching of the initial hollow bodies in a chromosulfuric acid bath, cleaning in a cleaning bath and noble metal activation in a Pd-bearing activation bath in a current-less procedure, while the subsequent deposition of the Ag-layer is effected electrolytically.

In that case the hollow body fill is accommodated in each case in an immersion drum with a suitably fine-mesh wall.

5 In a third embodiment the hollow bodies exclusively consist of an Ni- or Ni/Ag-metal casing with a wall thickness of between 4 and 5 μm and they are formed by the application of a metal layer to plastic particles of suitable diameter and subsequent removal of the plastic core by pyrolysis.

10 The invention is not limited in terms of its implementation to the preferred embodiments set forth hereinbefore. On the contrary, it is possible to envisage a large number of alternative configurations which make use of the principles set forth in accordance with the accompanying claims even in configurations of different kinds.

CLAIMS



1. Electrically conductive filler for a conductive plastic material, comprising particles with a highly conductive metal casing, characterised in that the particles are in the form of gas-filled and compression-elastic, in particular compressible, micro-hollow bodies.

2. A filler as set forth in claim 1 characterised in that the micro-hollow bodies have an inner casing of plastic material and are substantially gas-tight.

3. A filler as set forth in claim 1 or claim 2 characterised in that the micro-hollow bodies are of a diameter in the range of between 5 μm and 100 μm , in particular between 15 μm and 50 μm .

4. A filler as set forth in one of the preceding claims characterised in that at least a partial quantity of the micro-hollow bodies is of an approximately hollow spherical shape.

5. A filler as set forth in one of the preceding claims characterised in that at least a partial quantity of the micro-hollow bodies is of an approximately ellipsoidal, cylindrical or prismatic configuration, wherein the length of the longest major axis of an ellipsoid is at least 1.5 times the next larger major axis or the height of the cylinder is at least 1.5 times the radius or the height of the prism is at least 1.5 times the length of the greatest base surface side thereof.

6. A filler as set forth in one of the preceding claims characterised in that the metal casing covers substantially the entire surface of the micro-hollow bodies and in particular gas-tightly encloses same.





7. A filler as set forth in one of the preceding claims characterised in that the metal casing comprises at least two layers.

8. A filler as set forth in one of the preceding claims characterised in that the metal casing has a rough surface, in particular with a substantially radially oriented crystallite structure.

9. A filler as set forth in one of the preceding claims characterised in that the metal casing is of a mean thickness in the range of between 0.1 μm and 5 μm , wherein the mean thickness is so matched to the dimensions of the micro-hollow bodies that the effective density of the micro-hollow bodies is in the range of between 0.3 and 3 g/cm^3 .

10. A process for the production of a filler as set forth in one of the preceding claims characterised in that the operation of forming the conductive casing is effected by means of a current-less and/or an electrolytic liquid phase metallization procedure.

11. A process as set forth in claim 10 characterised in that the operation of forming the conductive casing includes a first step of forming a first metallization layer in a current-less metallization process and a second step of forming a second metallization layer in an electrolytic metallization process.

12. A process for the production of a filler as set forth in one of claims 1 through 9 characterised in that the operation of forming the conductive casing is effected by means of a gaseous phase metallization process, in particular vacuum vapor deposition or reactive sputtering.

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13. A process as set forth in one of claims 10 through 12 characterised in that at least one step of superficial cauterizing or etching of the surface of the micro-hollow bodies is effected before and/or after the formation of the conductive coating.



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