

Claims

1. Process for the preparation of hollow spherical glass particles comprising at least SiO₂, Al₂O₃, and an alkali metal oxide, comprising at least the steps of
 - 5 (I) preparing precursor-particles by a process comprising at least the following sub-steps
 - (I-1) providing a starting composition comprising particles of at least one starting compound for forming a glass which comprises at least SiO₂, Al₂O₃, and an alkali metal oxide,
 - 10 (I-2) mixing the starting composition with a liquid, thereby obtaining a slurry, and
 - (I-3) spray drying the obtained slurry, thereby obtaining the precursor-particles, and
 - (II) heat-treating the precursor-particles at a temperature from 1000°C to 1800°C by passing the precursor-particles through a heating device, thereby obtaining hollow
 - 15 spherical glass particles,

wherein at least one naked flame fed by a flammable gas is burning in the interior of the heating device and the heat-treatment is carried out by contacting the precursor-particles with the naked flame(s).
- 20 2. Process according to claim 1, where the hollow spherical glass particles comprise at least 30 wt.-% of SiO₂, at least 25 wt.-% of Al₂O₃, and at least 18 wt.-% of the alkali metal oxide, in each case based on the overall weight of the hollow spherical glass particles.
- 25 3. Process according to claims 1 or 2, wherein the alkali metal oxide is Na₂O.
4. Process according to any of claims 1 to 3, wherein the hollow spherical glass particles are free of boron.
- 30 5. Process according to any of claims 1 to 4, wherein the average diameter of the hollow spherical glass particles is from 20 μm to 200 μm.
6. Process according to any of claims 1 to 5, wherein the starting composition comprises at least a zeolite.
- 35 7. Process according to any of claims 1 to 5, wherein the starting composition comprises at least a zeolite, a clay and an alkali metal carbonate.
8. Process according to any of claims 1 to 7, wherein the temperature of the heat-treatment
- 40 is from 1300°C to 1600°C.

9. Process according to any of claims 1 to 8, wherein the contact time with the flame(s) is 0.001 s to 1s.
- 5 10. Process according to any of claims 1 to 9, wherein the heating device has a longitudinal reaction chamber.
11. Process according to claim 10, wherein the reaction chamber is cylindrical.
- 10 12. Process according to claims 10 or 11, wherein the inner hydraulic diameter of the longitudinal reaction chamber is from 0.1 to 3 m.
13. Process according to any of claims 1 to 12, wherein the precursor-particles are dispersed in the flammable gas which feeds the flame(s) in the heating device.
- 15 14. Process according to any of claims 1 to 12, wherein the precursor-particles are dispersed in a non-flammable gas which is added into the heating device at a position upstream of the flame(s).
- 20 15. Process according to any of claims 1 to 14, wherein the hollow spherical glass particles obtained are cooled after being in contact with the naked flame(s) in at least one cooling zone by at least one method selected from
- introducing a gas into the reaction chamber, and
 - cooling the walls of the reaction chamber.
- 25 16. Process according to claim 15, wherein the reaction chamber comprises at least two cooling zones.
- 30 17. Process according to any of claims 1 to 9, wherein the heating device used for step (II) comprises at least
- an inlet for a flammable gas,
 - an inlet for a non-flammable gas,
 - a longitudinal reaction chamber comprising at least two different zones (a) and (b), wherein
- 35 (a) is a combustion zone capable of being heated by at least one naked flame, wherein at least one burner nozzle which is connected with the inlet of the flammable gas is arranged in the combustion zone,
- (b) is a cooling zone, and
- an outlet for the hollow spherical glass particles, non-flammable gas and waste,
- 40 and step (II) is carried out as follows:

- (II-1) introducing a stream of the flammable gas through the inlet, transferring it to the burner nozzle(s) and igniting at least one naked flame,
- (II-2) introducing a stream of the non-flammable gas through the inlet into the combustion zone (a) and transferring it through the cooling zone (b) to the outlet,
- 5 (II-3) adding the precursor-particles into the heating device and contacting them with the naked flame(s) in the combustion zone (a) by at least one method selected from
- adding the precursor-particles to the stream of the flammable gas, and/or
 - adding the precursor-particles to the stream of the non-flammable gas,
- 10 thereby obtaining a stream of hollow spherical glass particles, waste-gas generated by combustion of the flammable gas and non-flammable gas,
- (II-4) cooling the formed stream of hollow spherical glass particles, waste-gas and non-flammable gas by passing them through the cooling zone (b), and
- (II-5) separating the hollow spherical glass particles from the waste-gas and the non-
15 flammable gas.
18. Process according to claim 17, wherein the longitudinal reaction chamber is in vertical orientation, wherein the combustion zone (a) is at its lower end and the cooling zone (b) is at its upper end.
- 20 19. Process according to claims 17 or 18, wherein the inner walls of the reaction chamber in the combustion zone (a) are protected by a refractory material.
20. Process according to claim 19, wherein the refractory material is cooled.
- 25 21. Process according to any of claims 17 to 20, wherein the combustion zone (a) comprises a plurality of nozzles for flammable gas.
22. Process according to claim 21, wherein the plurality of nozzles is arranged in such a
30 way, that flames are present in the entire cross section of the combustion zone (a).
23. Process according to any of claims 17 to 22, wherein the cooling zone (b) comprises means for additionally entering a cooling gas into the cooling zone.
- 35 24. Process according to any of claims 17 to 23, wherein the walls of the cooling zone (b) are cooled by means of a non-flammable gas.
25. Process according to any of claims 17 to 24 wherein the reaction chamber comprises at
40 least two cooling zones and cooling is carried out in at least two steps.

26. Process according to any of claims 17 to 25, wherein step (II-5) is carried out by means of a cyclone.
27. Process according to any of claims 17 to 26, wherein at least a part of the mixture of waste gas formed in course of combustion and non-flammable gas separated in course of step (II-5) is recirculated.
28. Process according to any of claims 1 to 9, wherein the heating device used for step (II) comprises at least
- an inlet for a flammable gas,
 - optionally an inlet for a non-flammable gas,
 - a cylindrical, rotatable reaction chamber which is rotatably mounted at its ends in a fixed front unit and a fixed rear unit, wherein the rotatable, cylindrical reaction chamber is arranged horizontal or inclined towards its rear end, and wherein the rotatable, cylindrical reaction chamber comprises at least two different zones (a) and (b), wherein
 - (a) is a combustion zone capable of being heated by least one naked flame, wherein at least one burner nozzle which is connected with the inlet for the flammable gas is arranged in the combustion zone, and
 - (b) is a cooling zone,
 - a fixed front unit comprising at least a mounting for the cylindrical, rotatable reaction chamber, an inlet for a stream of a flammable gas which is connected with the burner nozzle arrange in zone (a), and optionally an inlet for a non-flammable gas,
 - a fixed rear unit comprising at least a mounting for the cylindrical, rotatable reaction chamber, an outlet for hollow spherical glass particles and an outlet for waste gas, and
 - a drive for rotating the cylindrical, rotatable reaction chamber around its longitudinal axis
- and step (II) is carried out as follows:
- (II-0') rotating the cylindrical, rotatable reaction chamber around its longitudinal axis,
 - (II-1') introducing a stream of the flammable gas through the inlet, transferring it to the burner nozzle(s) and igniting at least one naked flame,
 - (II-2') optionally introducing a stream of a non-flammable gas through the inlet into the combustion zone (a) and transferring it through the cooling zone (b) to the outlet,
 - (II-3') adding the precursor-particles into the heating device and contacting them with the naked flame(s) in the combustion zone (a) by

- adding the precursor-particles to the stream of the flammable gas, and/or
 - adding the precursor-particles to the stream of the non-flammable gas,
- thereby obtaining hollow spherical glass particles in a waste gas stream,
- (II-4') cooling the hollow spherical glass particles in the waste gas stream by passing
5 them through the cooling zone (b) by means of the rotational movement o, and
- (II-5') removing the hollow spherical glass particles through the outlet hollow spherical
glass particles of the fixed rear unit and/or by separating the hollow spherical
glass particles from the waste gas flow exiting through the waste gas outlet.
- 10 29. Process according to claim 28, wherein the inclination angle of the cylindrical, rotatable
reaction chamber is from more than 0 to 10°.
30. Process according to claims 28 or 29, wherein the inner walls of the reaction chamber in
the combustion zone (a) are protected by a refractory material.
- 15 31. Process according to any of claims 28 to 30, wherein the combustion zone (a) comprises
a plurality of nozzles for flammable gas.
32. Process according to claim 31, wherein the plurality of nozzles is arranged in such a
20 way, that flames are present in the entire cross section of the combustion zone (a).
33. Process according to any of claims 28 to 32, wherein the cooling zone (b) comprises
means for entering a cooling gas into the reaction chamber.
- 25 34. Process according to any of claims 28 to 33, wherein step (II-5) is carried out by means
of a cyclone.
35. Process according to any of claims 28 to 34, wherein the mixture of waste gas formed in
course of combustion and non-flammable gas separated in course of step (II-5) is
30 recirculated.
36. Heating device for heat-treating precursor-particles comprising SiO_2 , Al_2O_3 , and an alkali
metal oxide at a temperature from 1000 to 1800°C thereby obtaining hollow spherical
glass particles, comprising at least
- 35 • a longitudinal reaction chamber comprising at least two different zones (a) and
(b), wherein
 - (a) is a combustion zone capable of being heated by least one naked flame,
wherein at least one burner nozzle which is connected with an inlet for the
flammable gas is arranged in the combustion zone,
 - 40 (b) is a cooling zone, and

- an inlet for the flammable gas,
 - an inlet for introducing a non-flammable gas into the combustion zone (a),
 - means for adding precursor-particles comprising SiO_2 , Al_2O_3 , and an alkali metal oxide to the flammable gas and/or the non-flammable gas,
- 5 • an outlet for removing hollow spherical glass particles, non-flammable gas and waste from the cooling zone (b).
37. Heating device according to claim 36, wherein the inner walls of the reaction chamber in the combustion zone (a) are protected by a refractory material.
- 10 38. Heating device according to claim 37, wherein the heating device comprises means for cooling the refractory material.
- 15 39. Heating device according to any of claims 36 to 38, wherein the combustion zone (a) comprises a plurality of nozzles for flammable gas.
- 20 40. Heating device according to claim 39, wherein the plurality of nozzles is arranged in such a way, that flames are present in the entire cross section of the combustion zone (a).
- 25 41. Heating device according to any of claims 36 to 40, wherein the cooling zone (b) comprises means for additionally entering a cooling gas into the cooling zone.
42. Heating device according to any of claims 36 to 41, wherein the walls of the cooling zone (b) double-walled and comprising at least an inlet and an outlet for a cooling gas.
43. Heating device according to any of claims 36 to 42, wherein the heating device comprises a cyclone which is connected with the outlet.
- 30 44. Heating device for heat-treating precursor-particles comprising SiO_2 , Al_2O_3 , and an alkali metal oxide at a temperature from 1000 to 1800°C thereby obtaining hollow spherical glass particles, comprising at least
- an inlet for a flammable gas,
 - optionally an inlet for a non-flammable gas,
- 35 • a cylindrical, rotatable reaction chamber which is rotatably mounted at its ends in a fixed front unit and a fixed rear unit, wherein the rotatable, cylindrical reaction chamber is arranged horizontal or inclined towards its rear end, and wherein the rotatable, cylindrical reaction chamber comprises at least two different zones (a) and (b), wherein

- (a) is a combustion zone capable of being heated by least one naked flame, wherein at least one burner nozzle which is connected with the inlet for the flammable gas is arranged in the combustion zone, and
- (b) is a cooling zone,
- 5 • a fixed front unit comprising at least a mounting for the cylindrical, rotatable reaction chamber, an inlet for a stream of a flammable gas which is connected with the burner nozzle arrange in zone (a), and optionally an inlet for a non-flammable gas,
- 10 • a fixed rear unit comprising at least a mounting for the cylindrical, rotatable reaction chamber, an outlet for hollow spherical glass particles and an outlet for waste gas, and
- a drive for rotating the cylindrical, rotatable reaction chamber around its longitudinal axis.
- 15 45. Heating device according to claim 44, wherein the inclination angle of the cylindrical, rotatable reaction chamber is from more than 0 to 10°.
46. Heating device according to claims 44 or 45, wherein the inner walls of the reaction chamber in the combustion zone (a) are protected by a refractory material.
- 20 47. Heating device according to any of claims 44 to 46, wherein the combustion zone (a) comprises a plurality of nozzles for flammable gas.
48. Heating device according to claim 47, wherein the plurality of nozzles is arranged in such a way, that flames are present in the entire cross section of the combustion zone (a).
- 25 49. Heating device according to any of claims 44 to 48, wherein the cooling zone (b) comprises means for entering a cooling gas into the reaction chamber.
- 30 50. Heating device according to any of claims 44 to 49, wherein the heating device comprises a cyclone which is connected to the outlet for waste gas.
51. Use of hollow spherical glass particles comprising at least SiO₂, Al₂O₃, and an alkali metal oxide as filler for high temperature products, molten metal, injection moulded synthetic materials, flame-retardant insulating foams, cement slurries, mortars, concretes and oil field applications, wherein the hollow spherical glass particles are manufactured by a process according to any of claims 1 to 35.
- 35 52. Use of hollow spherical glass particles comprising at least SiO₂, Al₂O₃, and an alkali metal oxide as additive for molten metals having a melting point of at least 500°C, wherein the hollow spherical glass particles are manufactured by a process according to any of claims 1 to 35.
- 40