(I-1) providing a starting composition comprising particles of at least one starting compound for forming a glass which comprises at least SiO_2, Al_2O_3, and an alkali metal oxide,

(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 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),

wherein the precursor-particles are dispersed in the flammable gas which feeds the flame(s) in the heating device and/or 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), and

wherein the hollow spherical glass particles comprise 0.1 wt.% or less of boron or are free of boron.

In another aspect, there is provided a process for the preparation of hollow spherical glass particles comprising at least SiO_2, Al_2O_3, and an alkali metal oxide, comprising at least the steps of

(III) preparing precursor-particles by a process comprising at least the following sub-steps

(I-4) providing a starting composition comprising particles of at least one starting compound for forming a glass which comprises at least SiO_2, Al_2O_3, and an alkali metal oxide,

(I-5) mixing the starting composition with a liquid, thereby obtaining a slurry, and

(I-6) spray drying the obtained slurry, thereby obtaining the precursor-particles, and

(IV) 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 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),

wherein the precursor-particles are dispersed in the flammable gas which feeds the flame(s) in the heating device and/or 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),

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 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.

In another aspect, there is provided a 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

- 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,
  - (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, wherein the precursor-particles are dispersed in the flammable gas which feeds the flame(s) in the heating device and/or 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),
- an outlet for removing hollow spherical glass particles, non-flammable gas and waste from the cooling zone (b),
- wherein the heating device additionally comprises at least one feature selected from:
  I) the combustion zone comprises flow straighteners, and
  II) the reaction chamber comprises lead-in tubes, which are arranged in a way that they direct part of the gas stream towards the interior of the reaction chamber and part flows essentially parallel to the wall.

In another aspect, there is provided a 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,
- 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.

It was an objective of the present invention to provide an improved process of manufacturing hollow spherical glass particles, which also allows manufacturing hollow spherical glass particles in heating-devices having large inner diameters.

Claims

1. Process for the preparation of hollow spherical glass particles comprising at least SiO_2, Al_2O_3, and an alkali metal oxide, comprising at least the steps of

(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 SiO_2, Al_2O_3, and an alkali metal oxide,

(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 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),

wherein the precursor-particles are dispersed in the flammable gas which feeds the flame(s) in the heating device and/or 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), and

wherein the hollow spherical glass particles comprise 0.1 wt.% or less of boron or are free of boron.

2. Process according to claim 1, wherein the heating device has a longitudinal reaction chamber.

3. Process according to claim 2, wherein the reaction chamber is cylindrical.

4. Process according to any of claims 1 to 3, 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.

5. Process according to claim 1, 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
  - (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,

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,

(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,

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-flammable gas.

6. Process according to claim 5 wherein the reaction chamber comprises at least two cooling zones and cooling is carried out in at least two steps.

7. Process for the preparation of hollow spherical glass particles comprising at least SiO_2, Al_2O_3, and an alkali metal oxide, comprising at least the steps of

(III) preparing precursor-particles by a process comprising at least the following sub-steps

(I-4) providing a starting composition comprising particles of at least one starting compound for forming a glass which comprises at least SiO_2, Al_2O_3, and an alkali metal oxide,

(I-5) mixing the starting composition with a liquid, thereby obtaining a slurry, and

(I-6) spray drying the obtained slurry, thereby obtaining the precursor-particles, and

(IV) 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 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),

wherein the precursor-particles are dispersed in the flammable gas which feeds the flame(s) in the heating device and/or 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),

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 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.

8. Process according to claim 7, wherein the combustion zone (a) comprises a plurality of nozzles for flammable gas.

9. Process according to claim 8, 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).

10. Process according to any of claims 7 to 9, wherein the mixture of waste gas formed in course of combustion and non-flammable gas separated in course of step (II-5') is recirculated.

11. 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

- 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,
  - (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, wherein the precursor-particles are dispersed in the flammable gas which feeds the flame(s) in the heating device and/or 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),
- an outlet for removing hollow spherical glass particles, non-flammable gas and waste from the cooling zone (b),
- wherein the heating device additionally comprises at least one feature selected from:
  I) the combustion zone comprises flow straighteners, and
  II) the reaction chamber comprises lead-in tubes, which are arranged in a way that they direct part of the gas stream towards the interior of the reaction chamber and part flows essentially parallel to the wall.

12. Heating device according to claim 11, wherein the walls of the cooling zone (b) double-walled and comprising at least an inlet and an outlet for a cooling gas.

13. 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,

- 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.

14. Heating device according to claim 13, wherein the combustion zone (a) comprises a plurality of nozzles for flammable gas.

15. Heating device according to claim 14, 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).