which preferably have a particle size from 10 µm to 600 µm. The heating device is a tube furnace comprising an outer heating mantle.

Our older application WO 2020/020921 A1 discloses a boron-free hollow spherical glass particle comprising at least 30 wt.-% of Al_2O_3, at least 35 wt.-% of SiO_2 and at least 18 wt.-% of at least one alkali metal oxide and having a particle diameter in the range from more than 20 µm to 75 µm. The application furthermore discloses a method of manufacturing such particles by providing a composition comprising at least 30 wt.-% of Al_2O_3, at least 35 wt.-% of SiO_2 and at least 18 wt.-% of at least one alkali metal oxide, wherein the components are present as fine particles having a particle size of ≤ 10 µm, mixing the particles with water and optionally an organic binder, spray drying the particles and feeding the dried particles into a heating device, for example a tube furnace, such that the particles are blown upwards while the temperature is maintained above 1000°C, thereby obtaining hollow spherical glass particles. Alternatively, two heating devices connected in series may be used or at least a part of the particles is cycled back into the heating device. The tube furnaces described comprise an outer heating mantle.

JP-A-7-277768 discloses a method for manufacturing hollow glass spheres. As starting material a mixture of a glass powder and an inorganic material, preferably a carbonate or a sulfate powder which decomposes at higher temperatures thereby generating a gas is used. The mixture is converted to granules, for example by means of a spray dryer and the granules are thereafter supplied into an air stream of a temperature sufficient to decompose the inorganic material to generate a gas. Preferably, the heat treatment is carried out for 5 to 1000 ms in an air steam of about 1200 to 1600°C. In example 1, a glass powder (55% of SiO_2, 14% of Al_2O_3, 8% of B_2O_3, 1% of MgO, 21% of CaO and 1% of BaO; wt.-percentages) is mixed wth $CaSO_4 * 2 H_2O$ and water to obtain a slurry which was spray dried to obtain granules with an average particle size of 50 µm. Thereafter, the granules were supplied into a gas burner air stream having a maximum temperature of 1500°C, heat-treated for about 100 milliseconds, and then collected by means of cyclone. The example does not teach, that the granules are brought into contact with the naked flames of the gas burner but only that the granules are fed to a hot air stream generated by the gas burner. No details about the the device used for heating the granules in a hot air stream have been disclosed.

Tube furnaces comprising an outer heating mantle for heat-treating materials at temperatures above 1000°C may be suitable if the diameter of the tube is not too large. However, with increasing diameter of the tube -as it may be necessary for production plants- heat transfer into the tube becomes increasingly difficult.

In an aspect of the present disclosure, 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

(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).

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).

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.