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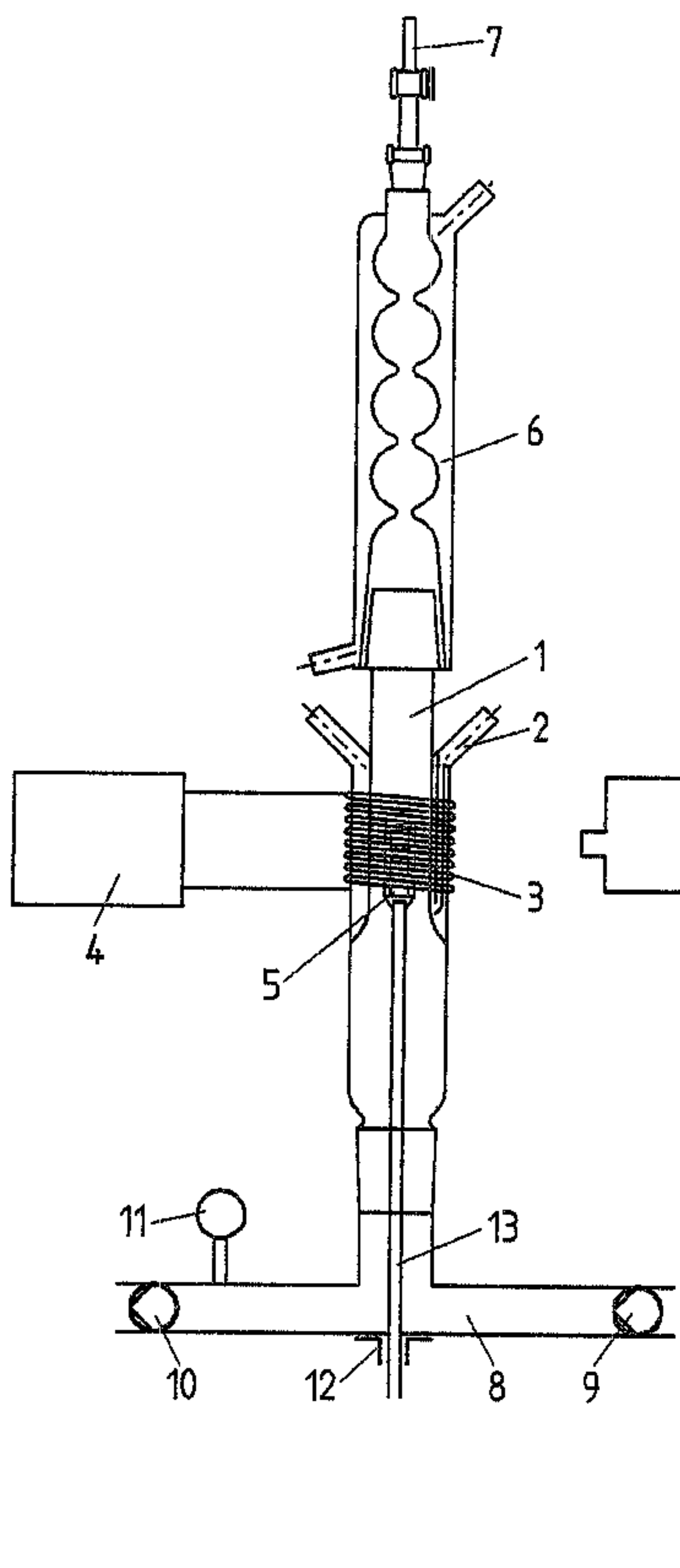
(54) Titre : PROCEDE POUR LA PREPARATION DE FULLERENES ET D'HETEROFULLERENES
(54) Title: PROCESS FOR THE PREPARATION OF FULLERENES AND HETEROFULLERENES



(57) Abrégé/Abstract:
There is described a process for the preparation of fullerenes and heterofullerenes - in the latter the carbon is partly replaced by boron and nitrogen - which comprises vaporizing shaped carbon pieces or shaped carbon pieces in contact with shaped boron nitride pieces in an inert gas atmosphere under reduced pressure in an inductive heating zone and depositing the vaporized portions on a cold surface as fullerene-containing soot and isolating fullerene or heterofullerene in a purification step from the soot using a solvent.

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Process for the preparation of fullerenes and heterofullerenes

Abstract of the disclosure:

There is described a process for the preparation of fullerenes and heterofullerenes - in the latter the carbon is partly replaced by boron and nitrogen - which comprises vaporizing shaped carbon pieces or shaped carbon pieces in contact with shaped boron nitride pieces in an inert gas atmosphere under reduced pressure in an inductive heating zone and depositing the vaporized portions on a cold surface as fullerene-containing soot and isolating fullerene or heterofullerene in a purification step from the soot using a solvent.

The invention relates to a process for the preparation of fullerenes. Fullerene is the name given to carbon clusters having a molecular size of C_{28} to C_{98}, in particular C_{60} to C_{70}. Heterofullerene is a carbon cluster in which all or some of the carbon is replaced by boron and nitrogen.

Fullerenes are solids and represent a third allotropic form of carbon besides graphite and diamond, which differs from the known forms by its molecular structure. The prototype C_{60} was given the name buckminsterfullerene and has the shape of a football made up of twelve pentagons (C_5 ring) and twenty hexagons (C_6 ring). Fullerenes are solids which can be sublimed and have limited solubility in organic solvents, giving a red-brown solution. Although the preparation of macroscopic amounts (0.1 - 1 g) of fullerenes was described for the first time in 1990 by W. Krätschmer et al., Solid C_{60}: a new form of carbon, Nature, Vol. 347 (1990), 354-358, a wide range of applications (lubricants in the form of miniaturized ballbearings, battery raw material due to its redox behavior, photocatalysis due to excitation to the triplet state of C_{60} by light of wavelength 450 nm, diamond synthesis, occlusion compounds) has already opened up. Metallic conductors and even superconductors having superconductive transition temperatures of 18 K (K_3C_{60}) and 28 K (Rb_3C_{60}) can be obtained from the insulator C_{60} by reaction with alkali metals, see Nature, Vol. 350 (1991), 320 and 600.

Furthermore, a wide range of applications has opened up for fullerenes and heterofullerenes due to the great variety of possible electrocyclic reactions, since C_{60} behaves like an olefin.

The wide range of applications of fullerenes and heterofullerenes has triggered a high demand for the substances themselves and also for simple preparation processes.

The preparation of fullerene has until now been based on noncontinuous electric-arc processes in which graphite is vaporized by the method of quasi-contacting resistance heating, Chem. Phys. Lett., Vol. 170 (1990) 167; Nature, Vol. 347 (1990), 354. Other preparation processes for fullerene utilize the laser vaporization method, Nature, Vol. 318 (1985), 162. Finally, Chem. Phys. Lett., Vol. 137 (1987), 306 describes the isolation of fullerene from the soot of optimized flames.

The object of the present invention is to describe a process for the preparation of fullerene and hetero-fullerene in which carbon is partly replaced by boron and nitrogen, with increased space-time yield, which can be extended to a continuous preparation process.

The object is achieved by vaporizing shaped carbon pieces or shaped carbon pieces in contact with shaped boron nitride pieces in an inert gas atmosphere under reduced pressure in an inductive heating zone and depositing the vaporized portions on a cold surface as fullerene-containing soot and isolating fullerene or hetero-fullerene in a purification step from the soot using a solvent.

The process of the invention can furthermore comprise the following optional steps of

a) using shaped carbon pieces made of graphite, isostatically compressed high-purity graphite, pyrolytic graphite or of glassy carbon obtained from polymer precursors and containing residual hydrogen;

b) using the shaped carbon piece and the shaped boron nitride piece in the form of cylindrical tubes;

c) using cylindrical tubes having an inside diameter of 5 to 60 mm and a wall thickness of 1 to 25 mm as the shaped piece;

d) using solid shaped carbon pieces;

e) using slotted, laminated or cone-shaped carbon pieces;

f) operating under argon or helium at a pressure of 10 to 400 hPa, in particular 25 to 200 hPa, as the inert gas atmosphere;

g) arranging one or more insulating tubes around the shaped carbon piece at a distance;

h) selecting a distance of 0.5 to 20 mm between the shaped carbon piece and the insulating tubes;

i) using one or more boron nitride insulating tubes;

j) using one or more multi-slotted graphite insulating tubes;

k) operating in a high-frequency furnace as the inductive heating zone;

l) heating the shaped carbon piece to more than 2500°C, in particular to 2600 to 3500°C;

m) depositing the fullerene-containing soot on a water-cooled quartz glass tube as the cold surface;

n) extracting the fullerene or heterofullerene from the soot with toluene as the solvent;

o) introducing a long shaped carbon piece continuously into the inductive heating zone so that the vaporized carbon is replenished.

To optimize the process according to the invention, it is desired to bring the power input through the inductor of the high-frequency generator into line with the removal of heat via the cooling water of the cold surface. The yield of fullerene or heterofullerene is increased in particular by arranging a single or multiple insulating tube made of pyrolytic boron nitride around the shaped carbon piece, because this results in an increase in temperature on the shaped carbon piece and a decrease in temperature on the cold surface. The additional effect of the insulating tube could be due to the longer and hotter reaction zone, in which gas phase deposition of fullerenes on soot particles may possibly take place, or else a chimney effect may occur. However, soot deposits on the inner surface of the insulating tube are free from fullerenes.

The intimate contact of the shaped carbon piece with a shaped boron nitride piece results in a process for the preparation of heterofullerenes by co-sublimation.

The high-purity graphite type EK 966 and the pyrolytic graphite used were obtained from Ringsdorff, Bonn. The glassy carbon was purchased from Sigri, Meitingen. A high-frequency furnace from Hüttinger IG, Freiburg im Breisgau, and a high-frequency generator of the 15/400 type were used. Owing to the good heat conduction, the vaporization of solid shaped graphite pieces requires an increased power input. This heat conduction may be reduced by cutting slots or lamellae into the graphite. However, it is better to vaporize mechanically stable glass carbon tubes, the heat conduction of which is less than that of graphite tubes.

The temperature of the shaped piece is measured by a pyrometer. If boron nitride tubes are used, slots or holes are made for this purpose by milling.

To increase the yield, the apparatus is filled with rare gas and then evacuated to 10^{-3} hPa three times before the heating process. After the last evacuation, the apparatus is then heated at 900°C in vacuo and thereafter under a stream of rare gas at atmospheric pressure.

It has been found that helium at about 150 hPa gives higher yields of fullerene and heterofullerene than argon. At helium pressures of less than 100 hPa, the amounts of fullerene formed are barely noticeable. In an argon atmosphere, undesired bright white gas discharges often take place, as a result of which the formation of fullerene and heterofullerene is then reduced.

The general preparation of fullerene is illustrated in more detail with reference to the 2 attached Figures:

In quartz glass tube 1 equipped with water cooling 2, the inductive heating zone 5 is built up by means of inductor 3 in combination with high-frequency generator 4. A cooler 6 equipped with ventilation 7 is arranged on quartz glass tube 1. A T-piece 8 containing throttle valves 9 and 10, bosshead 12 and manometer 11 is arranged on the bottom of quartz glass tube 1. Throttle valve 9 reduces the rare gas flow; throttle valve 10 is connected to a vacuum pump and regulates the pressure in quartz glass tube 1 downstream from manometer 11. A copper tube 13, through which cooling water is passed and which allows reintroduction of longer shaped carbon pieces into the inductive heating zone 5, goes through bosshead 12. The temperature of the shaped carbon piece is measured by pyrometer 19.

The arrangement of the shaped carbon piece is shown in detail in Figure 2.

A copper block 14 is mounted on the upper end of the copper tube 13 as a support. The shaped carbon piece 15 is positioned on a support disc 16 which in turn rests on a support tube 17. The support tube 17 is supported by the copper block 14. The insulating tube 18, which can also be designed as a double-tube, is also supported by the copper block 14.

The following special structural components produce high yields of fullerene and heterofullerene:

1 Quartz glass tube diameter (inside): 50 mm.
Quartz glass tube diameter (outside): 70 mm.

3 Inductor: 10 windings of 6 mm Cu pipe,
Height 80 mm,
Inside diameter 71 mm.

4 High-frequency generator: 500 kHz,
Power output on terminals: 15 kW.

15 Shaped carbon piece:
Graphite tube, height: 25 mm,
Outside diameter; 22.5 mm,
Wall thickness: 2 mm.

16 Boron nitride support disc.

17 Boron nitride support tube:
Outside diameter: 25 mm,
Wall thickness: 1 mm.

18 Boron nitride insulating tube:
Outside diameter: 40 mm,
Wall thickness: 1 mm,
Height: 80 mm.

18 Additional boron nitride double insulating tube:
Outside diameter: 29 mm,
Wall thickness: 0.5 mm,
Height: 40 mm.

15 Shaped carbon piece in contact with a shaped boron nitride piece:
Solid glass carbon tube or graphite tube
Height: 25 mm,
Outside diameter: 27.5 mm,

Boron nitride tube

Inside diameter:	28 mm,
Wall thickness:	0.5 mm,
Height:	40 mm.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

We claim:

1. A process for the preparation of fullerenes or heterofullerenes containing boron and nitrogen, which comprises vaporizing shaped carbon pieces or shaped carbon pieces in contact with shaped boron nitride pieces in an inert gas atmosphere under reduced pressure in an inductive heating zone; depositing the vaporized portions on a cold surface as fullerene-containing soot; and isolating fullerene or heterofullerene in a purification step from the soot using a solvent.

2. The process as claimed in claim 1, wherein shaped carbon pieces made of graphite, isostatically pressed high-purity graphite, pyrolytic graphite or of glassy carbon obtained from polymer precursors and containing residual hydrogen are used.

3. The process as claimed in claim 1, wherein the shaped carbon piece and the shaped boron nitride piece are used in the form of cylindrical tubes.

4. The process as claimed in claim 3, wherein the shaped pieces used are cylindrical tubes having an inside diameter of 5 to 60 mm and a wall thickness of 1 to 25 mm.

5. The process as claimed in claim 1, wherein solid shaped carbon pieces are used.

6. The process as claimed in claim 1, wherein slotted, lamellated or cone-shaped carbon pieces are used.

7. The process as claimed in claim 1, wherein the inert gas used is argon or helium under a pressure of 10 to 400 hPa.

8. The process as claimed in claim 7, wherein the inert gas atmosphere has a pressure of 25 to 200 hPa.

9. The process as claimed in claim 1, wherein one or more insulating tubes are arranged around the shaped carbon piece at a distance.

10. The process as claimed in claim 9, wherein a distance of 0.5 to 20 mm between the shaped carbon piece and the insulating tubes is selected.

11. The process as claimed in claim 9, wherein the insulating tubes are made of boron nitride.

12. The process as claimed in claim 9, wherein one or more multi-slotted graphite insulating tubes are used.

13. The process as claimed in claim 1, wherein the reaction is carried out in a high-frequency furnace as the inductive heating zone.

14. The process as claimed in claim 1, wherein the shaped carbon piece is heated to temperatures above 2500°C.

15. The process as claimed in claim 14, wherein the shaped carbon piece is heated to 2600 to 3500°C.

16. The process as claimed in claim 1, wherein the fullerene-containing soot is deposited on a water-cooled quartz glass tube as the cold surface.

17. The process as claimed in claim 1, wherein the fullerene or heterofullerene is extracted from the soot using toluene as the solvent.

18. The process as claimed in claim 1, wherein a long shaped carbon piece is continuously introduced into the inductive heating zone so that the vaporized carbon is replenished.

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FIG. 1 2082775

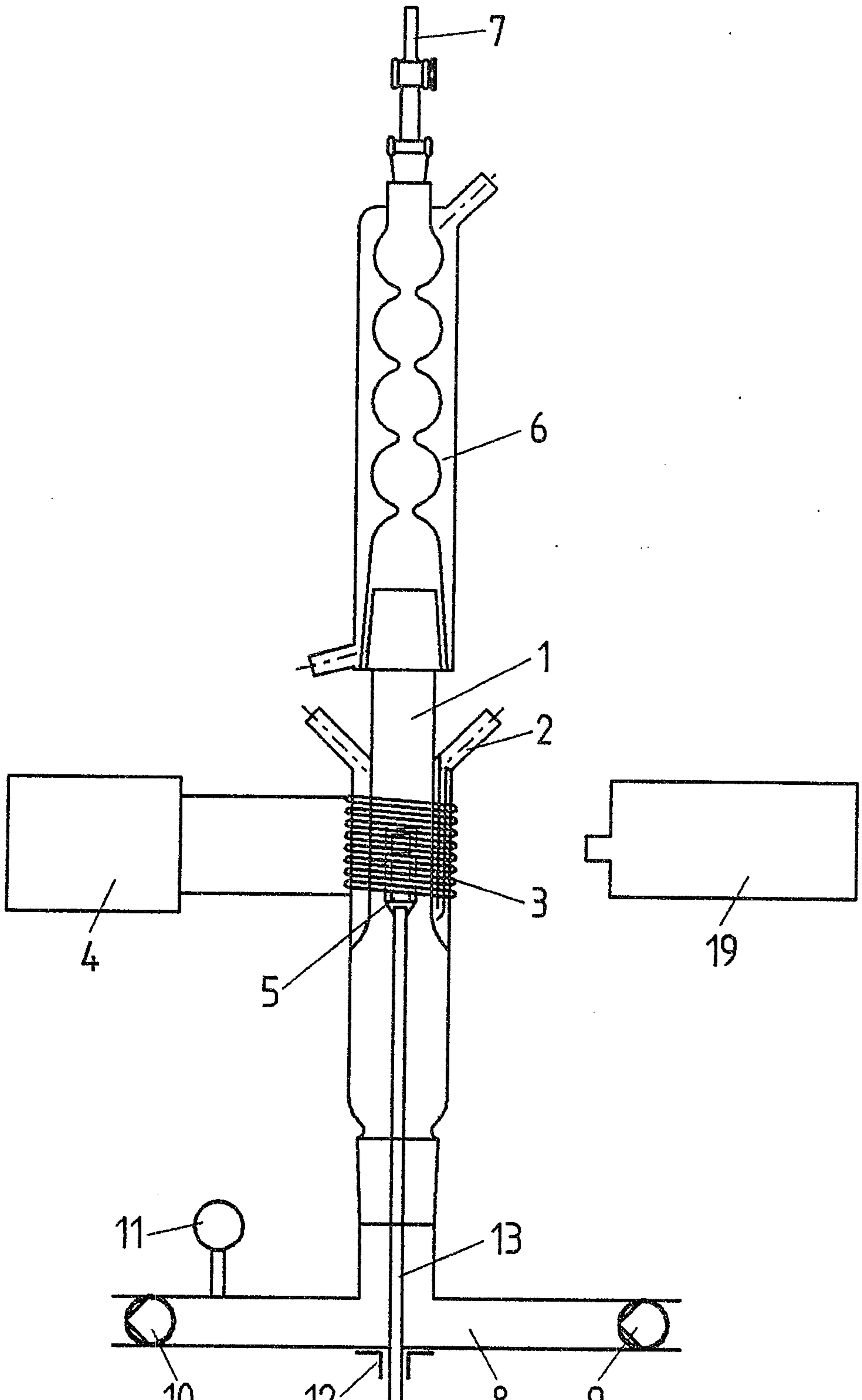

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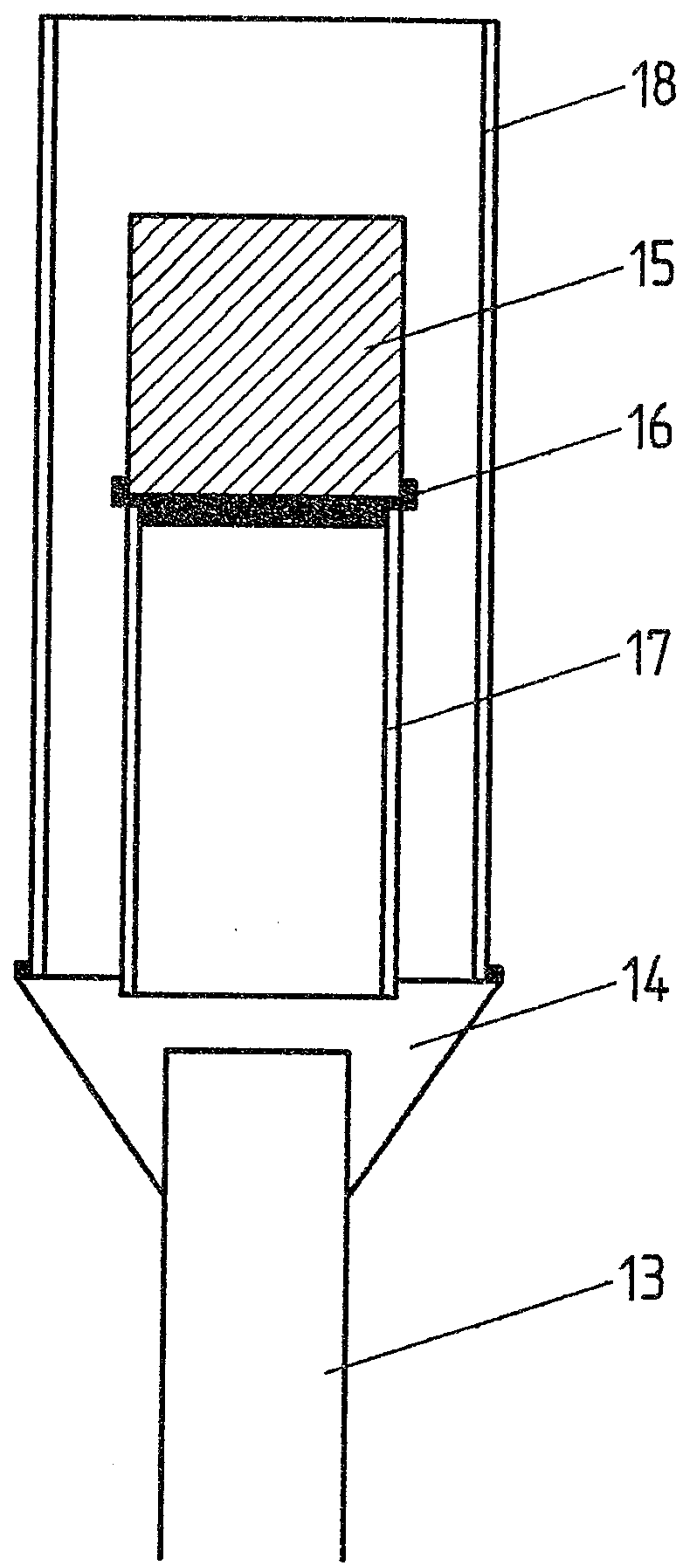
FIG. 2



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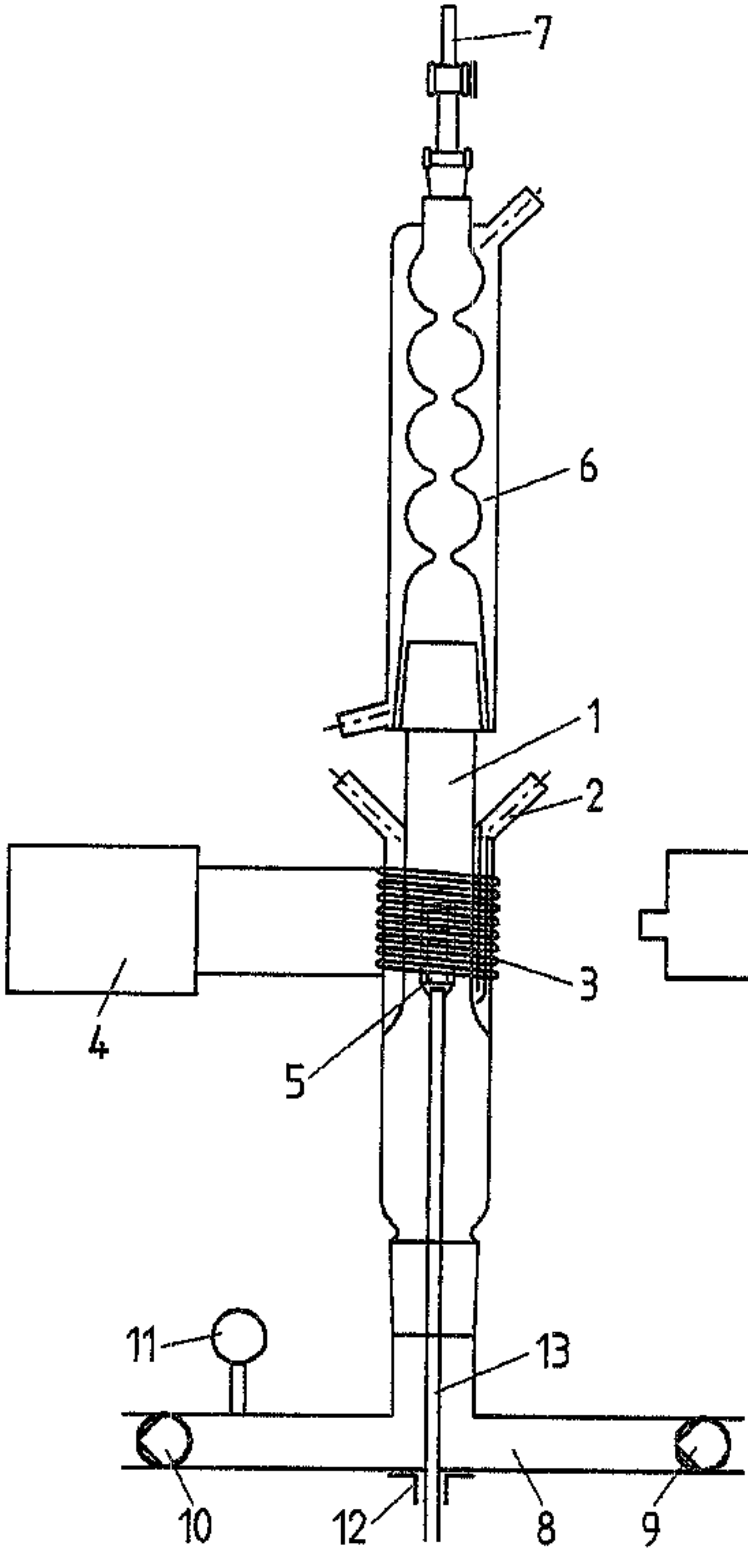
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