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Method and device for the elimination of volatile substances from high-viscous media

5 The invention relates to a continuous process for particularly gentle heating or concentration of polymer solutions or polymer melts, in particular of thermoplastic polymers, using a tube-bundle heat exchanger consisting of compact tubes having flat channels and a cross section variable over the length and a downstream separator, and an apparatus for carrying out this process.

10 The tube-bundle heat exchangers described in industry are used for heating or cooling fluids and for vaporizing volatile substances from viscous media. They usually consist of tubes with a circular cross section through which the medium to be devolatilized or to be heated flows and around the outside of which a heating medium flows. Fields of use of tube-bundle heat exchangers are, for example,
15 concentration plants for polymers, air conditioning systems or refrigerators.

For a few particular cases of use, tubes with a non-circular cross section were described. EP 0 772 017 A1 therefore describes a heat exchanger tube for use in tube-bundle heat exchangers, preferably in condensing boilers for cooling heating
20 gases. The tube has an approximately circular cross section at its ends and an oval or rectangular cross section in the tube part located in between, which cross section may be constant or variable. The inside of the tube is provided with beads, grooves or indentations in order to generate a turbulent boundary layer and to improve the heat transfer. However, the generation of turbulent flow with the aid of indentations, etc.
25 does not function in the case of the highly viscous polymer melts exhibiting laminar flow.

The tube-bundle heat exchanger apparatus described in EP 0218104 A1 operates in the low-pressure range according to the cross counterflow principle and is used for
30 gas/gas and liquid systems, in particular for combustion processes with large amounts of gas and high waste gas temperatures and for processes in which a solvent circulates. The apparatus consists of tubes which have a hexagonal cross-sectional profile at their ends and an elliptical or round cross section in the middle part (about



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90% of the tube length). The advantage of the hexagonal profile is that the tube ends can be joined directly to one another and a tight cavity thus forms between the tubes without preperforated end trays being required. However, this design is disadvantageous when the side walls of the heat exchanger jacket are connected to the joined tubes. It is necessary to weld on prepunched metal sheets which simulate the contour of the tubes joined to one another.

The heat exchanger described in DE 3 212 727 A1 and intended for cooling or heating highly viscous, in particular structurally viscous, flowable substances consists of rows of parallel tubes which are arranged offset by 90° in planes parallel to one another. The heating or cooling medium flows in the tubes, and the fluid to be heated or to be cooled flows on their outside, perpendicular to the plane of the rows of tubes. The tubes are in the form of round or flat tubes. A disadvantage of this arrangement is that many "dead spaces" exist between the intersecting tubes, in which dead spaces the medium to be heated or to be cooled collects and undergoes thermal decomposition. Moreover, this design is very complicated and difficult to scale up for larger production plants.

A brochure of Schrader Verfahrenstechnik GmbH discloses a flat-tube heat exchanger. This flat-tube heat exchanger is used for condensing vapors or as a heating element in concentration plants. The apparatus described is a tube-bundle heat exchanger which consists of a heat exchanger jacket in which flat tubes arranged in rows are present. Improved heat transfer and less fouling in comparison with round tubes are mentioned as advantages.

An application for polymers or polymer melts is not known.

Heat exchanger tubes having flat, oval or elliptical cross section and the production thereof are described in the prior art. DE 805 785 A1, for example, discloses a plate-type heating element which has a largely rectangular cross section. The plate-type heating element is however produced by bending over the two sides of a metal sheet and welding in further metal strips and stiffening profiles. This apparatus is taken as a basis in DE 2 506 434 A1, the heat exchanger tube being produced from a single

metal strip by bending over, and a supporting flange being integrated. The overlapping ends are then welded. A similar flat tube is described in DE 19 857 510, but here the supporting flange consists of an edge of the metal strip which is bent from the surface of the tube to the tube interior and back again so that two chambers
5 form. The publication DE 7 837 359 describes a flat heat exchanger tube which, in contrast to the abovementioned one, ensures strong and liquid-tight connection in the overlap region over the entire period of use of the tube.

A disadvantage of all designs mentioned is the complicated production of the tubes,
10 at least one shaping and one joining process being necessary. It is an object of the invention to use a compact tube in which only one shaping process is necessary. Moreover, it is intended to dispense with the joint seam, which can lead to disadvantageous changes in the melt flow.

15 It is the object of the invention to remove volatile substances from highly viscous polymer solutions under particularly gentle conditions, i.e. with as low a thermal load as possible (temperature and residence time) and narrow residence time distribution, and to provide a suitable apparatus which does not have the disadvantages of the known heat exchangers.

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The object is achieved, according to the invention, by passing the polymer solution continuously through a tube-bundle heat exchanger consisting of compact tubes and heating said solution to a temperature above the boiling point of the volatile substances. The volatile substances are then separated off in a downstream separator
25 (devolatilization chamber) from the polymer melt, and the devolatilized polymer melt is transported further through a discharge apparatus, for example a gear pump (e.g. for granulation).

The invention relates to an evaporator apparatus for the treatment of viscous media,
30 consisting at least of a feed chamber having a perforated tray, a tube-bundle heat exchanger connected thereto and having perpendicularly arranged tubes and a perforated ceiling (lower perforated tray), and a devolatilization chamber connected thereto and having a discharge unit for the product and a vapor take-off for removing

volatile components, characterized in that the tubes of the heat exchanger have a rectangular or elliptical cross section over one part of their longitudinal dimension, in particular over the greatest part of their longitudinal dimension.

- 5 In the context of the invention, the term rectangular cross section includes rectangular cross sections having rectangular and rounded edge shapes as well as the so-called "long circle", i.e. two parallel straight sides are joined together by arcs of a circle. The preferred configuration for the cross section is that of a long circle, of rectangular cross sections having rounded edges or elliptical cross sections, long
10 circles being especially preferred.

The tubes of the heat exchanger preferably have a rectangular or elliptical cross section over 70 to 98% of their longitudinal dimension.

- 15 The maximum thickness D (i.e. the extension of the cross section of the tube along the short axis of the cross section) of the tube interior in the region of the rectangular or elliptical cross section is preferably 1 to 50 mm, particularly preferably 1 to 20 mm.
- 20 The maximum width B (i.e. the extension of the cross section of the tube along the long axis) of the tube interior in the region of the rectangular or elliptical cross section is in particular 5 to 500 mm, preferably 7 to 100 mm, particularly preferably 7 to 50 mm.
- 25 The ratio of maximum width B to maximum thickness D is in particular 2:1 to 30:1, particularly preferably 4:1 to 10:1.

The tubes preferably have a length of 100 mm to 10 m, preferably of 200 mm to 3 m, particularly preferably of 500 mm to 1 m.

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In a preferred embodiment, the tubes have a wall thickness of 0.5 to 5 mm, preferably of 1 to 4 mm.

The tubes can be obtained, for example, by being formed from tubes having a circular cross section, for example by rolling or pressing.

5 Particularly preferably, vertical wires, chains, wire loops or wire braids are attached to the ends of the tubes of the heat exchanger, in the devolatilization chamber.

These serve as means for increasing the size of the phase boundary between, for example, polymer to be devolatilized and the gas space, in order to accelerate vapor expulsion processes.

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Suitable arrangements of wires, wire loops or wire braids are disclosed, for example, in DE 10 144 233 A1, the content of which is hereby incorporated by reference.

15 Sharp edges (corners) with possible dead corners for the product are avoided in the invention. The danger of nonuniform distribution of the product flow is less in an elliptical tube than in a flat tube.

20 The tube can be made circular in the usual manner at the tube ends, with the result that customary fastening in the plates of a tube-bundle heat exchanger is possible. Furthermore, product entrance and exit can then be designed in the usual manner. The transition from round to elliptical or rectangular cross section preferably takes place without sharp edges.

25 In a particularly preferred variant of the invention, the tube may have a plurality of zones of different cross-sectional area. The flattening can be effected in two or more stages.

30 It is furthermore possible to introduce additional orifice plates in the region of the tube end, which are intended to keep the pressure in the tube interior at the same level at the end of the tubes. This prevents nonuniform evaporation behavior in the evaporator tubes arranged side by side. Consequently, maldistribution is prevented.

A variant of the apparatus in which a cross-sectional constriction which in particular

extends over not more than half, preferably not more than a third, particularly preferably not more than a fourth, of the length of the tube (8) and in particular over at least two hundredths, preferably at least one hundredth, particularly preferably at least one fiftieth, of the length of the tube (8) is provided in the upper entrance region
5 of the tubes (8) is also preferred (cf. for example fig. 5).

An apparatus which is characterized in that the length of the cross-sectional constriction corresponds at least to its internal diameter, particularly preferably is at least twice as long, is particularly preferred.
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Compared with apertures, an abrupt drop in the pressure and sudden vaporization of any solvent is prevented. The comparatively larger diameter compared with aperture arrangements prevents the danger of blockage in the region of the constriction.

15 The further advantages of such an arrangement are that improved admission pressure can be established in the feed chamber and hence a uniform distribution of the polymers over the various heat exchanger tubes is possible.

Very particularly preferred is an apparatus of said type which is characterized in that
20 the cross-sectional constriction is formed by an inserted sleeve in the tubes.

It may be advantageous to utilize the poorer heat transfer between such an inserted sleeve in the entrance region of the tubes to keep the temperature difference between entering product stream and the inner surface of the sleeve smaller than the
25 temperature difference which results during operation of the apparatus without an inserted sleeve. This effect can be enhanced by using a material having a comparatively lower thermal conductivity for the inserted sleeve than for the tubes and by leaving an open gap between heat exchanger tube and inserted sleeve or by increasing the wall thickness of the inserted sleeve.

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The invention according to the invention also relates to the use of the evaporator apparatus according to the invention for removing volatile components from polymer solutions or melts.

The invention furthermore relates to a process for evaporating volatile components from polymer solutions or melts using an evaporator apparatus according to the invention, comprising the steps of preheating the polymer to a temperature of 150 to 250°C, preferably of 160 to 240°C, passing the polymer into the feed chamber at a
5 pressure of 2000 to 100 000 hPa, preferably of 5000 to 50 000 hPa, passing the polymer through the tube bundle of the heat exchanger with heating of the tubes, preferably by means of a heat exchange medium flowing countercurrent to the polymer, to a temperature of 160 to 380°C, preferably 165 to 300°C, and evaporation and removal of the volatile compounds in the region of the devolatilization chamber
10 and optionally additionally in the lower section of the tubes at a pressure in the devolatilization chamber of 1 to 5000 hPa, preferably of 2 to 2500 hPa, particularly preferably of 5 to 1000 hPa, and collecting and discharging the polymer.

A preferred process is characterized in that the evaporation and removal of the
15 volatile compounds are additionally effected in the lower quarter, in particular in the lower eighth, of the tubes.

Preferably, the viscosity of the polymer material on entering the feed chamber is 100 mPa·s to 10^7 Pa·s, preferably 500 mPa·s to 10^6 Pa·s, particularly preferably
20 1 Pa·s to 10^5 Pa·s.

In particular, the throughput of polymer material, based on a single tube, is 0.5 to 12 kg/h, preferably 1 to 9 kg/h.

25 The devolatilization can be carried out in one or more stages, in the latter case it being possible to connect a plurality of tubular heat exchangers in series or to combine them with other devolatilization apparatuses.

The tubes of the tube-bundle heat exchanger are produced, for example, from round
30 tubes, which are brought into the shape shown in fig. 1 with the aid of a suitable tool, for example a roll. The tubes have a cross section which changes over the length. The two ends have the in particular original round cross section of the starting tube, which, for example, has a diameter in the range of 6 mm to 450 mm, preferably of

6 mm to 50 mm, in particular of 10 mm to 40 mm. This permits fastening in conventional perforated trays using the conventional automated welding methods. The cross section in the middle region of the tube corresponds approximately to that of a flat rectangular channel having round or elliptical side walls (cf. fig. 2). The flat
5 tubes have no seam since they are produced from one piece.

Preferably, the process according to the invention is used for heating or for devolatilizing thermoplastic polymers as a melt or solution. These polymers include all plastics which are flowable under the influence of pressure and temperature.
10 Polycarbonate, polyamide, polypropylene, polyethylene, polyester, polystyrene, hydrogenated polystyrene, polyurethane, polyacrylate, polymethyl methacrylate, poly(styrene/acrylonitrile), poly(acrylonitrile/butadiene/styrene) and their copolymers or optionally blends of the polymers may be mentioned here by way of example. The substances and volatile compounds to be devolatilized are all solvents
15 which can expediently be combined with the abovementioned polymers, or monomers thereof or low molecular weight oligomers, for example chlorobenzene, methylene chloride, bisphenol A, caprolactam, styrene, acrylonitrile, toluene, ethylbenzene and cyclohexane.

20 When the tubular heat exchanger is used as an evaporator, the mixture enters the tube bundle as a single phase. Evaporation is permitted by a pressure gradient in the tubes, and, at the end of the apparatus, the mixture, in the form of a gas/liquid mixture, enters the separating container (devolatilization chamber), where the volatile compounds are removed as a gas. The devolatilized melt is further transported, for
25 example via a pump, to the next devolatilization stage or a granulation apparatus.

When the compact-tube heat exchanger is used as a pure heat exchanger, the tube heating is adjusted so that the product temperature of the mixture flowing in the tubes remains below the boiling point of the lowest-boiling volatile substance at the
30 prevailing pressure.

The heating medium has, for example, a temperature of between 50°C and 350°C. The exact heating temperature depends on the polymer solution to be heated or

concentrated and on the desired result of concentration or on the desired product temperature.

The pressure drop established over the tube length is not more than 100 000 hPa.

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Stainless steels, nickel-based alloys, titanium, aluminum and other alloys are suitable as material for the evaporator apparatus. Low-iron stainless steels are preferably used.

10 The process according to the invention serves for removing volatile substances, such as solvents and monomers, from a polymer solution or for heating the polymer solution, said process being distinguished by the following advantages in comparison with the prior art:

15 - better heat transfer in the tubular heat exchanger between heating medium and product owing to the greater surface/volume ratio of the flat compact tubes in comparison with round tubes

- a shorter length of the heat exchanger owing to the better heat transfer

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- a shorter residence time in the tubular heat exchanger owing to the shorter length and reduced volume

25 - less material damage owing to the shorter residence time at high temperature and hence better quality of the end product, in particular of polymers (e.g. mechanical properties, color number, processability)

- lower capital costs owing to the compact design

30 - a more uniform distribution in the case of highly viscous polymer solution over the tube cross section or complete filling of the compact tubes in comparison with generally broader, known plate-type evaporator or plate-type heat exchanger.

Owing to the round cross section of the tube ends, connection to the conventional perforated trays in the region of the feed chamber and of the devolatilization chamber is possible. Moreover, simple scale up by numbering is achievable with such an apparatus.

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Fundamental investigations have shown that as low a thermal load as possible is required for gentle devolatilization of polymer melts, i.e. a long residence time at low temperature or a short residence time at high temperature and at the same time a narrow residence time distribution. For reasons relating to cost-efficiency, the latter is preferable. Experimental investigations into the evaporator apparatus according to the invention led to the result that these requirements are outstandingly fulfilled by such apparatuses and hence considerable savings in the capital costs of the plant are to be expected.

15 The process according to the invention is used, for example, in two areas:

- *Evaporation processes of volatile substances in chemical reactions:*

- 20 - separating off water or other low molecular weight substances in polycondensation reactions, for example in the preparation of esters, oligoesters, polyesters or polyamides
- separating off phenol in the condensation of diphenyl carbonate with aromatic bisphenols to give oligomers or polymers or
- 25 - reactions with formation of a component which can be separated off and has a high vapor pressure (HCl removal in the reaction of phosgene with alcohols to give dialkyl carbonates)
- 30 - pyrolysis reactions in which desired products vaporizable under pyrolysis conditions form, e.g. cleavage of polyesters due to macrocyclic mono- or dilactones

- pyrolysis reactions in which a reactive gaseous component is formed from the desired substance under pyrolysis conditions and is separated off, for example separation of gaseous alcohol from isocyanate obtained as condensate in the pyrolysis of urethanes

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- ***Evaporation processes without chemical reaction:***

- separating off volatile monomers (diisocyanates) from coating resins
- 10 - gentle solvent removal from mixtures containing thermally sensitive substances (in particular in the case of fine chemicals) and
- separation of solvents and of monomers from polymer solutions, in particular of chlorobenzene and/or methylene chloride from
- 15 polycarbonate melts, caprolactam from polyamide melts, styrene, acrylonitrile and toluene or ethylbenzene from SAN melts or ABS melts, cyclohexane from h-polystyrene melts
- separation of volatile desired substances from mixtures, for example
- 20 from distillation residues
- separation of ethanol from alcoholic beverages

25 The invention is explained in more detail below by way of example with reference to the figures and on the basis of an embodiment.

The figures show the following:

30 Figure 1: the side view of a heat exchanger tube 8 having a variable tube cross section over the length

Figure 2: the cross section of the flat tube section

Figure 3: the design of the tube-bundle heat exchanger

Figure 4: the schematic overall view of the evaporator apparatus according to the invention

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The evaporator apparatus 1 has the following design:

10 The heat exchanger tubes 8 arranged parallel to one another (cf. fig. 3) are present in a heat exchanger container 4 consisting of an outer jacket 10 and two perforated trays 3, 9 in which the tubes 8 are fastened in such a way that a gas-tight space forms. The tube ends are terminated by the perforated trays 3, 9. A heating medium flows around the outside of the tubes 8, countercurrently to the polymer solution in the tubes 8. In the middle region, the tubes 8 (cf. fig. 1) have the virtually rectangular cross-sectional shape shown on a larger scale in fig. 2. The short side edges of the
15 tubes 8 are, however, rounded. The heating oil flows into the chamber 4 at the inlet 12 and out of the chamber 4 again at the outlet 11.

Figure 4 shows the overall design of the evaporator apparatus. Above the upper perforated tray 3 is the feed chamber 2 with the feed pipe 13 for the polymer; the
20 devolatilization chamber 5 with the discharge pump 6 and the vapor take-off 7 thereof for the volatile component is mounted below the lower perforated tray 9 (perforated ceiling).

Example

Removal of volatile components from a polymer solution:

- 5 A preheated polymer solution consisting of about 80% of mass ABS and about 20% of monomer or solvent (acrylonitrile, styrene, ethylbenzene and methyl ethyl ketone) is transported via the feed chamber 2 with perforated tray 3 into a compact-tube heat exchanger having four tubes 8. The tubes have a total length of 1310 mm, the flat tube region being 1170 mm long and, in the rectangular region, having a slot
- 10 thickness D of 3 mm and a slot width B of 12 mm (cf. fig. 1). The tube 8 is heated with oil by the countercurrent method. The entry temperature of the polymer solution in the heat exchanger 4 is 194.7°C. The polymer solution flows with a polymer throughput of 6 kg/h downwards through the tubes 8 heated at 240°C and leaves the tube 8 at a temperature of 225.4°C. A pressure drop of 52.800 hPa is established over
- 15 the tube length. The volatile substances are separated from the melt in the devolatilization container 5 at 10 hPa.

- Comparative experiments using an evaporator having a round tube of the same length (diameter: 10 mm) showed that, with the same throughput, a heat transfer
- 20 which is better by the factor 1.8 can be realized with the tubular heat exchanger according to the invention. Moreover, it was possible to reduce the residual content of solvents by about 33% by weight using the compact-tube heat exchanger.

Patent Claims

1. An evaporator apparatus (1) for the treatment of viscous media, consisting at least of a feed chamber (2) having a perforated tray (3), a tube-bundle heat
5 exchanger (4) connected thereto and having perpendicularly arranged tubes (8) and a perforated ceiling (9) and a devolatilization chamber (5) connected thereto and having a discharge unit (6) for the product and a vapor take-off (7) for removing volatile components, characterized in that the tubes (8) of the heat exchanger (4) have a rectangular or elliptical cross section over one
10 part of their longitudinal dimension, in particular over the greatest part of their longitudinal dimension.
2. The evaporator apparatus as claimed in claim 1, characterized in that the tubes (8) of the heat exchanger (4) have a rectangular or elliptical cross
15 section over 80 to 98% of their longitudinal dimension.
3. The evaporator apparatus as claimed in claim 1 or 2, characterized in that the maximum thickness D of the tube interior in the region of the elliptical or rectangular cross section is 1 to 50 mm, preferably 1 to 20 mm.
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4. The evaporator apparatus as claimed in any of claims 1 to 3, characterized in that the maximum width B of the tube interior in the region of the rectangular or elliptical cross section is 5 to 500 mm, preferably 7 to 100 mm, particularly preferably 7 to 50 mm.
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5. The evaporator apparatus as claimed in any of claims 1 to 4, characterized in that the tubes (8) have a length of 100 mm to 10 m, preferably of 200 mm to 3 m, particularly preferably of 500 mm to 1 m.
- 30 6. The evaporator apparatus as claimed in any of claims 1 to 5, characterized in that the tubes (8) have a wall thickness of 0.5 to 5 mm, preferably of 1 to 4 mm.

7. The evaporator apparatus as claimed in any of claims 1 to 6, characterized in that those parts of the apparatus which are in contact with product, in particular the tubes (8), consist of a low-iron material, in particular selected from the series consisting of steel, nickel alloy, aluminum or titanium, in particular low-iron steel.
8. The apparatus as claimed in any of claims 1 to 7, characterized in that vertical wires, chains, wire loops or wire braids are mounted at the ends of the tubes (8) of the heat exchanger (4), in the devolatilization chamber (5).
9. The apparatus as claimed in any of claims 1 to 8, characterized in that the tubes (8) have a plurality of zones having a different rectangular or elliptical cross-sectional area.
10. The apparatus as claimed in any of claims 1 to 9, characterized in that a cross-sectional constriction which in particular extends over not more than half, preferably not more than a third, particularly preferably not more than a fourth, of the length of the tube and in particular over at least two hundredths, preferably at least one hundredth, particularly preferably at least one fiftieth, of the length of the tube is provided in the upper entrance region of the tubes.
11. The apparatus as claimed in claim 10, characterized in that the length of the cross-sectional constriction corresponds at least to its internal diameter, preferably is at least twice as long.
12. The apparatus as claimed in either of claims 10 and 11, characterized in that the cross-sectional constriction is formed by an inserted sleeve (14) in the tubes (8).
13. The use of an evaporator apparatus as claimed in any of claims 1 to 9 for removing volatile components from polymer solutions or polymer melts.
14. A process for evaporating volatile components from polymer solutions or

- melts using an evaporator apparatus as claimed in any of claims 1 to 9, comprising the steps of preheating the polymer to a temperature of 150 to 250°C, preferably of 160 to 240°C, passing the polymer into the feed chamber (2) at a pressure of 2000 to 100 000 hPa, preferably of 5000 to 50 000 hPa, passing the polymer through the tube bundle of the heat exchanger (4) with heating of the tubes (8), preferably by means of a heat exchange medium flowing countercurrent to the polymer, to a temperature of 160 to 380°C, preferably 165 to 300°C, and evaporation and removal of the volatile compounds in the region of the devolatilization chamber (5) and optionally additionally in the lower section of the tubes (8) at a pressure in the devolatilization chamber (5) of 1 to 5000 hPa, preferably of 2 to 2500 hPa, particularly preferably of 5 to 1000 hPa, and collecting and discharging the polymer.
15. The process as claimed in claim 11, characterized in that the evaporation and removal of volatile compounds are additionally effected in the lower quarter, in particular in the lower eighth, of the tubes (8).
16. The process as claimed in claim 11 or 12, characterized in that the polymer is selected from the series: polycarbonate, polyamide, polypropylene, polyethylene, polyester, polystyrene, hydrogenated polystyrene, polyurethane, polyacrylate, polymethyl methacrylate, styrene/acrylonitrile, resin, poly(acrylonitrile/butadiene/styrene) and their copolymers or optionally blends of the polymers.
17. The process as claimed in any of claims 11 to 13, characterized in that the volatile compounds are solvents or monomers or low molecular weight oligomers of the polymers used, preferably chlorobenzene, methylene chloride, bisphenol A, caprolactam, styrene, acrylonitrile, toluene, ethylbenzene and cyclohexane.
18. The process as claimed in any of claims 11 to 14, characterized in that the viscosity of the polymer material on entering the feed chamber (2) is

100 mPa·s to 10^7 Pa·s, preferably 500 mPa·s to 10^6 Pa·s, particularly preferably 1 Pa·s to 10^5 Pa·s.

19. The process as claimed in any of claims 11 to 15, characterized in that the
5 throughput of polymer material, based on a single tube (8), is 0.5 to 12 kg/h, preferably 1 to 9 kg/h.