

Device and process for the removal of volatile components from polymer solutions

5 This invention relates to a device and a process for the removal of volatile constituents from polymers, in particular for vaporising volatile components from polymer solutions by indirect heat exchange. The device has at least one container with an inlet for the polymer solution and outlet for the volatile components and an outflow for the polymer from which the volatile components have been removed, and a heat exchanger with a plurality of channels, which form a heat exchange zone,
10 wherein the channels have a length of 1.0 to 40 cm, a height, constant over the length thereof, of 1.3 to 13 mm and a width of 1 to 10 cm in the entry zone of the channels and wherein the width of the channels at least doubles between the entry thereof and the exit thereof.

15 The removal of volatile components from a polymer solution is one of the final processing stages in the production of many polymers. The volatile constituents to be removed may be either solvents or unpolymerised monomers. Depending upon the viscosity of the polymer solution, various methods are known for the removal of the volatile components from polymer solutions, each involving heating the polymer
20 solution by means of a heat exchanger to a temperature above the vaporisation temperature of the volatile constituents. Drying devices which are described are, for example, film evaporators, extruders and those with indirect heat exchange.

25 It is vital during heating of the polymer solution that the polymer is not thermally degraded.

Published patent application EP-A-150225 describes an apparatus having two heat exchange bundles connected in series. The heat exchange bundles have rectangular channels. This apparatus is primarily used for two-stage heating or cooling during
30 the reaction, but is a relatively complex piece of equipment.

EP-B-226204 discloses a process and a heat exchanger for the removal of volatile constituents from a polymer solution containing at least 25 wt.% of polymer. The polymer solution is heated in an indirect heat exchange zone, which consists of a plurality of channels. The channels have a substantially uniform ratio of surface area to volume in the range from 0.158 to 1.97 mm⁻¹, a height of 1.27 to 12.7 mm, a width of 2.54 to 10.16 cm and a length of 1.27 to 30.48 cm. The polymer solution is heated in the channels at a pressure of 2-200 bar to a temperature above the vaporisation temperature of the volatile components, but below the boiling temperature of the polymer. The residence time of the polymer solution in the channels is 5 to 120 seconds. After heating, the solution is transferred into a chamber in which at least 25% of the volatile constituents are stripped from the solution. The process reduces thermal damage by reducing the time for which the polymer is exposed to elevated temperatures. One disadvantage of the process is, however, that it is not possible to achieve complete removal of the solvent in a single stage. Moreover, polymer deposits form on the outside of the heat exchange bundle which carbonise over time and occasionally flake off, so contaminating the polymer from which the solvent has been removed.

EP-B-352 727 discloses a process for the removal of volatile constituents from polymer solutions by heating the polymer solution to above the vaporisation temperature of the volatile components in a plurality of channels connected in parallel. The ratio of heat exchange surface area to the volumetric flow rate of the product is ~80 m²/m³/h. The flow velocity in the channels is ~0.5 mm/s and the residence time of the polymer solution in the channels is 120 to 200 seconds. This process also has the disadvantage that complete removal of the solvent is not possible in a single stage. Moreover, polymer deposits form on the outside of the heat exchange bundle which carbonise over time and occasionally flake off, so contaminating the polymer from which the solvent has been removed.

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The object thus arises of providing an apparatus and a process for the removal of volatile components from a polymer solution which do not exhibit the disadvantages of the prior art.

- 5 This object is achieved according to the invention by the provision of a device according to independent claim 1.

10 The present invention provides a device for the removal of volatile components from a polymer solution comprising at least one container, which has an inlet for the polymer solution, an outlet for the volatile components and an outflow for the polymer solution from which the volatile components have been removed, and a heat exchanger arranged inside the container which has a central receiving zone for the polymer solution, which is connected to the container inlet, a product zone to receive the treated polymer solution, a heat exchange unit having a plurality of
15 channels, which form a heat exchange zone and which connect the receiving zone to the product zone, a heating means to heat the heat exchange unit and the channels, characterised in that the channels have a length of 1.0 to 40 cm, a height, constant over the length thereof, of 1.3 to 13 mm and a width of 1 to 10 cm in the entry zone of the channels in the receiving zone, wherein the width of the channels at least
20 doubles between the entry thereof and the exit thereof to the product zone.

25 The channels preferably have a rectangular cross-section and the width of the channels at the outlet is three times as large as the width of the channels at the inlet, wherein the channels may widen continuously, but in accordance with any desired profile.

In a preferred embodiment, the channels widen parabolically.

30 A device in which the width of the channels is kept constant for at least half the length thereof and then widens to at least double the width, wherein the enlargement proceeds continuously, but in accordance with any desired, in particular non-linear,

profile is likewise preferred. When an appropriately adjusted temperature is used, the channel shapes ensure that the width of the channel is constant in the zone in which the polymer solution is heated and does not enlarge until the polymer solution has reached a temperature of above the vaporisation temperature of the volatile components, such that these may readily be stripped out of the solution while still in the channels.

In one variant, both the width and the height of the channel may widen towards the exit in the preferred manner.

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The heat exchanger of the device according to the invention preferably has at least 100 such channels. In particular, however, there are 200 to 100,000 channels in the heat exchanger.

15 In a preferred embodiment, the heat exchanger has a cylindrical shape, such that the channels surround the receiving zone in a cylindrical configuration. The heat exchanger is preferably arranged in the area of the channel outlets that the individual channels directly abut with each other laterally and/or at the upper and under side thereof, such that there are no zones between the channel exits on which the polymer material may be deposited. This applies to both the cylindrical and any other configuration of the channels.

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In another preferred embodiment of the device, the heat exchange unit in particular has a cuboid shape and is arranged beneath the receiving zone.

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In a preferred embodiment, the heat exchange unit is formed from a plurality of superposed or adjacent plate segments arranged in planes, wherein the plate segments are spaced apart in one plane, and wherein the spacing thereof and the lateral profile in the plane determine the width of the channels and the thickness of the plate segments determines the height of the channels.

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In a preferred variant of the device, the heat exchange unit is formed from a plurality of superposed or adjacent plates arranged in planes, which plates are separated by spacers, wherein the spacing and lateral profile of the spacers determine the width of the channels and the thickness of the spacers determines the height of the channels.

The device is preferably entirely or in part, in particular those parts in contact with the polymer solution, made from a metallic material having a low iron content which contains at most 10 wt.%, preferably at most 5 wt.% of iron.

The material having a low iron content is preferably tantalum or a nickel alloy having a low iron content and is in particular selected from the range Alloy 59 (2.4605), Inconell 686 (2.4606), Alloy-B2, Alloy-B3, Alloy-B4, Hastelloy C-22, Hastelloy-C276, Hastelloy-C4, preferably Alloy 59.

The heat exchanger has any desired means known to the person skilled in the art for heating the channels to temperatures above the vaporisation temperature of the volatile components. These means are, for example, resistance heaters or a network of tubes to convey a heat exchange fluid.

The channels in the heat exchange unit are preferably inclined over the length thereof by a downwards angle relative to the horizontal towards the exit thereof, in particular, they are arranged vertically. In this case, the receiving zone is arranged above the channels.

The heating means for the heat exchanger preferably comprise a plurality of tubes which pass transversely relative to the channels through the plate segments or through the plates and through which a heat exchange fluid circulates.

The present invention also provides a process for the removal of volatile components from a polymer solution containing at least 40 wt.% of polymer using the device according to the invention, wherein the process comprises:

- 5 A) introduction of the polymer solution into the receiving zone at a pressure of 1 to 100 bar abs.,
- B) passage and heating of the polymer solution in the channels of the heat exchanger to a temperature above the vaporisation temperature of the volatile
10 components of the polymer solution and below the boiling or decomposition temperature of the polymer, wherein the residence time of the polymer solution in the channels is from 5 to 120 sec,
- C) separation of the volatile components from the polymer solution through the
15 outlet and
- D) discharge of the polymer from which the volatile components have been removed.

20 The device and process according to the invention may be generally applied for the removal of volatile components from sensitive solids, in particular from thermoplastic polymers, elastomers, silicone polymers and high molecular weight lubricants and similar substances.

25 Preferably, however, the process according to the invention is used for degassing thermoplastic polymers. These polymers comprise any plastics which flow under the action of pressure and heat. Polystyrene, polycarbonate, polyphenylene, polyurethane, polyamide, polyester, polyacrylate, polymethacrylate may be mentioned by way of example in this connection. The process is very particularly
30 suitable for degassing polycarbonate.

The volatile components may be both unpolymerised monomers and solvents. One solvent frequently used in the production of thermoplastic polymers is, for example, methylene chloride, or a mixture of methylene chloride and chlorobenzene.

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The polymer solutions contain at least 40 wt.% of polymer. In the molten state, the polymer solution typically has a viscosity of 0.5 to 200 Pas.

10 In the process, the polymer solution is in particular compressed into the channels at a pressure of 1.5 to 50 bar abs., preferably of 2 to 5 bar abs., flows through the channels of the heat exchanger and is so heated to a temperature of preferably 250 to 350°C. The pressure prevailing at the outlet of the channels is preferably below the saturation pressure of the volatile components at the particular temperature. The pressure in the product zone is preferably less than or equal to 10^5 Pa, in particular
15 from 3000 Pa to 10^5 Pa.

Preferably, the pressures upstream and downstream from the channels, the temperature in the channels and the shape of the channels are selected such that the volatile components are already completely separated from the polymer in the
20 channels.

The pressure in the receiving zone and the temperature in the channels is in particular selected such that at least 95%, in particular at least 98%, preferably at least 99.5%, particularly preferably at least 99.8% of the volatile components of the
25 polymer solution vaporise in the channels.

The residence time of the polymer solution in the channels is typically 5 to 120 sec, preferably 80 to 120 sec. The flow velocity of the polymer solution is in particular from 0.0001 to 0.01 mm/s, preferably from 0.001 to 0.005 mm/s. The ratio of heat
30 exchange surface area of the channels to the volumetric flow rate of the polymer solution is 5 to 75, preferably 15 to 50 $\text{m}^2/\text{m}^3/\text{h}$.

The following Figures illustrate the invention in greater detail. These illustrations are provided merely by way of example and thus do not limit the invention.

- 5 Figure 1 shows a longitudinal section of an apparatus according to the invention.
- Figure 2 shows a preferred arrangement of the channel width.
- 10 Figure 3 shows a cross-section of one plane of the heat exchanger.
- Figure 4 shows in a longitudinal section through one part of a heat exchanger how the planes of the heat exchanger are superposed.
- 15 Figure 5 shows a cross-section through one part of a variant of the heat exchanger of a device according to the invention comprising superposed plate segments.
- Figure 6 shows a longitudinal section through a variant of the device according to the invention having vertically arranged channels.
- 20 Figure 7 shows a longitudinal section along line A-A in Figure 6 in simplified form to clarify the passage of the heat exchange medium through the tubes 13.

Examples

The apparatus according to the invention is represented in Figure 1. All units are made from Alloy 59 or have an Alloy 59 coating. The apparatus has a double shell 16. The upper part of the apparatus has an inlet 1 for the polymer solution and an outlet 3 for the volatile components. In the lower part, the polymer from which the volatile constituents have been removed is discharged through the outlet 2 with the assistance of pump 24. The temperature of the inlet 1 is controlled with a heat exchange medium.

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Inside the double shell 16 is located the heat exchanger 31 with a central receiving zone 21 to receive the polymer solution to be degassed. The receiving zone 21 is connected to the inlet 1. 200 channels 14 (*c.f.* Figure 2) are arranged around the receiving zone 21, which channels extend from the receiving zone to the periphery of the heat exchanger 31 and which flare parabolically towards the exit 32 into the product zone 18.

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The polymer solution is pumped through the inlet 1 into the receiving zone 21 using a conventional pump (not shown). In order to achieve a more uniform distribution of the polymer solution into the individual channels, a cylindrical displacement member 10 is located in the centre of the receiving zone 21. The heat exchanger furthermore has means to heat the channels to above the vaporisation temperature of the volatile components. These means are a plurality of tubes 13 on the periphery or within the heat exchanger 31, which are interconnected by the annular chamber 17. In the upper part, the tubes 13 are connected to the annular chamber 11, in which the hot heat exchange oil is introduced through line 4. The heat exchange oil is discharged from the heat exchanger through the line 5. The tubes 13 are held together by end plates. The shell 16 of the apparatus may be heated with a heat exchange fluid.

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Figure 2 is a schematic representation of a longitudinal section of a channel according to the invention of the device. The entry 23 has a rectangular cross-section with a height of 2 mm and a width of 10 mm. The length of the channel is 110 mm. The width of the channel is a constant 10 mm for the first 60 mm. Thereafter, the channel widens, such that the width thereof at the exit 32 is 40 mm. The downstream portion of the side walls 25 and 26 of the channel 14 is parabolic in shape.

Figure 3 shows how the channels 14 according to the invention are arranged in a circular configuration around the receiving zone 21. The tubes 13 run through the holes 22 in the spacers 20.

Figure 4 shows a longitudinal section of several superposed channel planes. The channels 14 are formed by a plurality of alternately superposed spacers 20 and plates 19, through which the tubes 13 pass and hold the spacers and the plates in position. The arrangement shown here is suitable for a device having a vertical position of the channels 14. The receiving zone 21 in this case is located above the channel entries 23.

In the variant shown in **Figure 5**, the heat exchange unit 32 is formed by layers 37 of superposed plate segments 36. The segments 36 are spaced apart by a layer 37 and so form the width of the channels 14. The height of the channels 14 is defined by the thickness of the plate segments 36.

The functioning of the apparatus according to the invention is further illustrated by means of **Figure 1**. Once the polymer solution to be treated has been conveyed into the receiving zone 21, the solution passes into the channels 14, in which it is heated and the volatile components are removed therefrom. At the end 32 of the channels 14, the degassed polymer falls due to gravity into the product zone 18 of the shell 16 and is conveyed out of the apparatus according to the invention by means of pump 24 via line 2. The volatile components are drawn off through the outlet 3. The

channels are heated by a heat exchange fluid, which circulates in the lines 4, 13 and 5.

5 In the variant of the device according to Figure 6 (longitudinal section), vertically arranged layers of rectangular plates 19 and spacers 20 (*c.f.* Figure 4) are held together by a bundle of tubes 13, the ends of which are connected by tube bends (not shown) and form a tubing system. The tubing system is connected to the inlet tube 4 and the outlet 5 for passage of a heat exchange oil (*c.f.* Figure 7).

10 The polymer solution enters the device through the inlet 1 (Figure 6), passes through the receiving zone 21 with the displacement member 10 and is distributed among the channels 14. In the channels 14, the solution flows downwards and the volatile constituents are removed by heating. The polymer melt leaves the channels 14 and drips into the product zone 18 for further processing. The polymer is discharged by
15 means of the pump 24 through the line 2.

Test Example

In this Example, a 75 wt.% polycarbonate solution containing 24 wt.% of
20 chlorobenzene and 1 wt.% of methylene chloride was concentrated in an apparatus as shown in Figure 1. The polycarbonate solution was compressed into the channels 14 at a pressure of 3000 hPa and heated therein to 300°C. A pressure of 40 hPa prevailed in the product zone downstream from the channels. The residence time of the polymer in the channels 14 was 100 seconds. The channels were 1 cm wide at
25 the entry 23 and 3 cm wide at the exit 32 and, after half the channel length, flare out as shown in Figure 2. All parts in contact with the product were made from Alloy 59. The pressures at the entry 23 and exit 32 of the channels 14 and the shape of the channels were selected such that the volatile components have already completely or at least virtually completely been removed in the channels. The degassed
30 polycarbonate exhibited a residual chlorobenzene content (solvent) of only 400 ppm.

**Patent Claims:**

1. Device for the removal of volatile components from a polymer solution comprising at least
5 a container (30), which has an inlet (1) for the polymer solution, an outlet (3) for the volatile components and an outflow (2) for the polymer solution from which the volatile components have been removed,
10 and a heat exchanger (31), which is arranged inside the container (30), with a central receiving zone (21) for the polymer solution, which is connected to the container inlet, a product zone (18) to receive the treated polymer solution,
15 a heat exchange unit (32) having a plurality of channels (14), which form a heat exchange zone and which connect the receiving zone to the product zone (18),
20 a heating means (13) to heat the heat exchange unit (32) and the channels, characterised in that the channels (14) have a length of 1.0 to 40 cm, a height, constant over the length thereof, of 1.3 to 13 mm and a width of 1 to 10 cm in the entry zone of the channels (14) in the receiving zone (21), wherein the width of the channels (14) at least doubles between the entry (23) thereof and exit (32) thereof to the product zone (18).
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2. Device according to claim 1, characterised in that the width of the channels (14) at least triples between the entry (23) thereof and the exit (32) thereof to the product zone (18).
- 30 3. Device according to claim 1 or 2, characterised in that the width of the channels (14) is constant between the entry (23) thereof and at least half the



length thereof and at least doubles, preferably at least triples, over the remainder of the length thereof to the exit (32) to the product zone (18).

4. Device according to one of claims 1 to 3, characterised in that the width of the channels (14) increases non-linearly, in particular parabolically, between the entry (23) thereof and the exit (32) thereof to the product zone (18).
5. Device according to one of claims 1 to 4, characterised in that the heat exchanger (31) has more than 100, preferably from 200 to 100,000 channels.
6. Device according to one of claims 1 to 5, characterised in that the heat exchange unit (32) has a cylindrical shape and surrounds the receiving zone (21).
7. Device according to one of claims 1 to 5, characterised in that the heat exchange unit (32) in particular has a cuboid shape and is arranged beneath the receiving zone (21).
8. Device according to one of claims 1 to 7, characterised in that the heat exchange unit (32) is formed from a plurality of superposed or adjacent plate segments (36) arranged in planes (37), wherein the plate segments (36) are spaced apart in one plane (37), and wherein the spacing thereof and the lateral profile in the plane determine the width of the channels (14) and the thickness of the plate segments (36) determines the height of the channels (14).
9. Device according to one of claims 1 to 7, characterised in that the heat exchange unit (32) is formed from a plurality of superposed or adjacent plates (19) arranged in planes (37), which plates are separated by spacers (20), wherein the spacing and lateral profile of the spacers (20) determine the



width of the channels (14) and the thickness of the spacers (20) determines the height of the channels (14).

- 5 10. Device according to one of claims 1 to 9, characterised in that the channels (14) in the heat exchange unit (32) are inclined over the length thereof by a downwards angle relative to the horizontal towards the exit (32) thereof, in particular, they are arranged vertically.
- 10 11. Device according to one of claims 1 to 10, characterised in that the heating means (13) comprise a plurality of tubes (13), which pass transversely relative to the channels (14) through the plate segments (36) or through the plates (19) and through which a heat exchange fluid circulates.
- 15 12. Device according to one of claims 1 to 11, characterised in that the device is entirely or in part, in particular those parts in contact with the polymer solution, made from a metallic material having a low iron content which contains at most 10 wt.%, preferably at most 5 wt.% of iron.
- 20 13. Device according to claim 12, characterised in that the material having a low iron content is tantalum or a nickel alloy having a low iron content and is in particular selected from the range Alloy 59 (2.4605), Inconel 686 (2.4606), Alloy-B2, Alloy-B3, Alloy-B4, Hastelloy C-22, Hastelloy-C276, Hastelloy-C4, preferably Alloy 59.
- 25 14. Process for the removal of volatile components from a polymer solution containing at least 40 wt.% of polymer using a device according to claims 1 to 13 by
 - 30 A) introduction of the polymer solution into the receiving zone (21) at a pressure of 1 to 100 bar abs.,



- 5 B) passage and heating of the polymer solution in the channels (14) of the heat exchanger (31) to a temperature above the vaporisation temperature of the volatile components of the polymer solution and below the boiling or decomposition temperature of the polymer, wherein the residence time of the polymer solution in the channels is from 5 to 120 sec,
- 10 C) separation of the volatile components from the polymer solution through the outlet (3)
- D) discharge of the polymer from which the volatile components have been removed.
- 15 15. Process according to claim 14, characterised in that the polymer is a thermoplastic polymer, preferably polystyrene, polyphenylene, polyurethane, polyamide, polyester, polyacrylate, polymethacrylate, polycarbonate or a copolymer of the stated polymers, in particular polycarbonate, or is an elastomer or a silicone polymer.
- 20 16. Process according to one of claims 14 or 15, characterised in that the volatile component is a polymer solvent or a monomer of the polymer.
- 25 17. Process according to one of claims 14 to 16, characterised in that the pressure in the receiving zone (21) and the temperature in the channels (14) are selected such that at least 95%, in particular at least 98%, preferably at least 99.5%, particularly preferably at least 99.8% of the volatile components of the polymer solution vaporise in the channels.
- 30 18. Process according to one of claims 14 to 17, characterised in that the temperature in the channels (14) is 250 to 350°C.



19. Process according to one of claims 14 to 18, characterised in that the pressure in the receiving zone (21) at the entry (23) to the channels (14) is from 1.5 to 50 bar abs., preferably from 2 to 5 bar abs..

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20. Process according to one of claims 14 to 19, characterised in that the pressure in the product zone (18) is less than or equal to 10^5 Pa, in particular from 3000 Pa to 10^5 Pa.