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(54) Title: OLEFIN POLYMERIZATION PROCESS

(57) Abstract: The present invention relates to an olefin polymerization process comprising polymerization of at least one olefin monomer in one or more polymerization reactors. An object of the present invention is to recover unreacted components from the polymer powder leaving the reactor of an olefin polymerization process. Another object of the present invention is to reduce the amount of dissolved monomers with higher molecular weight to prevent issues with fouling and lump formation in subsequent purging operations.

Title: Olefin polymerization process

Description:

The present invention relates to an olefin polymerization process comprising polymerization of olefin monomer(s) in one or more polymerization reactors.

Processes for vapor-phase polymerization of monomers in a vapor-phase, quench-cooled reactor vessel are known in the art.

Polyolefins, such as polyethylene and polypropylene, may be prepared by particle form polymerization, also referred to as slurry polymerization. In this technique, a monomer feed may be polymerized in a reaction zone in the presence of a catalyst and optionally, a solvent (also known as a diluent) to produce a polymerization effluent containing a slurry of polymer solids in a liquid medium comprising unreacted hydrocarbon monomer and optionally, solvent. In order to recover the polymer solids from the slurry, the polymerization effluent may be withdrawn from the reactor and the polymer solids may be separated from the liquid medium. Typical polymer recovery and separation systems include subjecting the polymerization effluent to a reduction in pressure so that the liquid medium may vaporize leaving concentrated polymer solids. The vaporized liquid medium may exit at an upper portion of a flash tank, while the polymer solids may be recovered through a lower portion of the flash tank. The vaporized liquid medium can then be recycled back to the reaction zone.

WO 2017/102303 in the name of the present applicant relates to an olefin polymerization process comprising polymerization of at least one olefin monomer in one or more polymerization reactors wherein the polymerization process is carried out in an apparatus comprising one or more reactor vessels to which olefin monomer and catalyst components can be added and which contain an agitated bed of forming polymer particles, means for removing a stream comprising polymer particles from the reactor, means for removing a gas-liquid stream comprising unreacted olefin monomers from the reactor, means for withdrawing a liquid recycle stream from the gas-liquid stream, means for recycle a gas-liquid stream to the reactor, wherein the process further comprises the steps of withdrawing a gaseous stream from the stream comprising polymer particles, contacting a liquid recycle stream with the gaseous

stream thereby forming a mixture, withdrawing a liquid stream from the mixture and recycling a vapor stream from the mixture to the polymerization reactor.

US Patent No. 4,921,919 relates to a method and apparatus for minimizing the formation of polymer agglomerates or lumps in a reactor used in the gas-phase polymerization of polypropylene. In operation of vapor-phase polymerization processes using vapor-phase, quench-cooled reactor vessels such processes and apparatus, particles of polymer are formed around solid catalyst particles. The horizontally disposed reactor vessel typically has recycled propylene gas introduced into the bottom thereof together with hydrogen gas. Then, liquid propylene, as a quench liquid, is injected into the reactor from the top of the reactor. The hydrogen is provided for molecular weight control. Agitators inside the vessel stir the contents of the vessel. At a so-called upstream end of the vessel a catalyst system comprising a catalyst injected at one point into the top of the vessel, and a cocatalyst plus modifier injected at a point adjacent the point of injection of the catalyst, is injected into the top of the vessel. Solid polypropylene powder is created in the vessel and is withdrawn from the downstream end thereof.

EP 1 853 635 relates to a process for the polymerization of ethylene in which the ethylene is polymerized in the presence of a catalyst in a gas-phase reactor to form polymer particles and reaction gas comprising propane and unpolymerized ethylene is circulated to remove the heat of polymerization, wherein the polymer particles are discharged continuously or discontinuously from the reactor, the polymer particles are separated from the major part of the concomitantly discharged gas and the polymer particles are degassed, the gas is freed of entrained fine particles, the gas is separated from a low-boiling fraction comprising in a first separation stage, a propane fraction is separated off in a second separation stage and this propane fraction is used for degassing the polymer particles discharged from the reactor.

EP 2 083 020 relates to a process for the recovery of unreacted monomers from a polyolefin polymerization process, comprising the steps of recovering a fluid stream generated by the separation of the polyolefin product from the polymerization fluid comprising unreacted monomers and optionally comonomers, contacting said fluid stream in an absorption zone with a scrub liquid, thereby absorbing at least a portion of the unreacted monomers in said scrub liquid; and withdrawing from said absorption zone a vapor overhead comprising light gas and an absorber bottoms scrub liquid

comprising said unreacted monomer and thereby recovering said unreacted monomer in said absorber bottoms scrub liquid.

WO 2019/027565 relates to a method for separating gaseous unreacted hydrocarbon monomer and/or solvent from polyolefin solids, wherein the method consists essentially of contacting a first stream comprising the polyolefin solids and the gaseous unreacted hydrocarbon monomer and/or solvent with a first purge gas in a gas-solid separation vessel to separate the gaseous unreacted hydrocarbon monomer and/or solvent from the polyolefin solids to produce a second stream comprising polyolefin solids substantially free of gaseous unreacted hydrocarbon monomer and/or solvent and a third stream comprising the gaseous unreacted hydrocarbon monomer and/or solvent, wherein the first purge gas comprises hydrocarbon monomer and/or solvent and has a temperature of at least about 70°C when entering the gas-solid separation vessel.

WO 2019/027566 relates to a method for separating gaseous unreacted hydrocarbon monomer and/or solvent from polyolefin solids, wherein the method consists essentially of flowing a first stream comprising polyolefin solids and gaseous unreacted hydrocarbon monomer and/or solvent through a portion of a gas-solid separation vessel having a volume sufficient so that polyolefin solids present in the first stream have a residence time within the gas-solid separation vessel > about 5.0 minutes to separate gaseous unreacted hydrocarbon monomer and/or solvent from the polyolefin solids to produce a second stream comprising polyolefin solids substantially free of gaseous unreacted hydrocarbon monomer and/or solvent and a third stream comprising the gaseous unreacted hydrocarbon monomer and/or solvent.

According to the existing technology as discussed above there is a liquid purge from the reactor outlet streams. Such a purge or a liquid bleed from the reactor may contain unreacted valuable components and these valuable components would also be lost via that liquid bleed.

The present inventors found that when producing polypropylene or polyethylene copolymers with 1-hexene (C6) or 1-butene (C4), a large amount will remain dissolved in the polymer powder leaving the reactor. For safety and product quality reasons, these components need to be removed from the polymer powder, typically using purging with nitrogen. In addition, for example hexene is a valuable component and that component need to be recovered from this stream as well. The recovery of these

valuable components is most effectively done before the purge column, because at that stage the monomers need to be separated from a large amount of nitrogen, which involves additional costs.

Furthermore, the present inventors found that when the powder temperature is increased to improve the efficiency of the subsequent purging operation, dissolved monomers with higher molecular weight may cause plasticizing of the polymer material. Such a plasticizing action will make the polymer material more sticky and soft leading to issues with fouling and lump formation in subsequent purging operations.

An object of the present invention is to recover unreacted components from the polymer powder leaving the reactor of an olefin polymerization process.

Another object of the present invention is to reduce the amount of dissolved monomers with higher molecular weight to prevent issues with fouling and lump formation in subsequent purging operations.

The present invention thus relates to a process for polymerization of olefins, such as propylene, ethylene and 1 -hexene, in the presence of a catalyst system in a reactor comprising an agitated bed for forming polymer particles, a plurality of liquid feed ports, and a plurality of gas feed ports, wherein the process comprises the steps of:

- recovering a reactor off-gas comprising H2, olefins from the reactor,
- feeding the reactor off-gas to a condenser to form a gas-liquid mixture,
- feeding the gas-liquid mixture to a separator to obtain a first gas stream comprising H2, ethylene and propylene and a first liquid stream comprising H2, ethylene, propylene and 1 -hexene, wherein fresh propylene is further fed to the separator and/or added to the first liquid stream,
- feeding the catalyst system to the reactor through a port arranged on the top side of the reactor,
- feeding a H2 poor quench liquid comprising propylene a H2 rich quench liquid comprising H2, ethylene and propylene and 1 -hexene to the reactor through the liquid feed ports,
- feeding a H2 poor bottom gas comprising fresh propylene and a H2 rich bottom gas comprising H2, ethylene and propylene through the gas feed ports,
- collecting the polymer particles formed in the agitated bed from the reactor,

- feeding fresh ethylene and fresh C4-C8 olefin to the reactor, wherein the step of collecting the polymer particles formed in the agitated bed from the reactor comprises a step of contacting the stream of polymer particles with a stripping gas thereby forming a stream of polymer particles having a C4-C8 olefins content that is lower than the C4-C8 olefins content of the stream of polymer particles formed in the agitated bed from the reactor,

-compressing and recycling the stripping gas to the reactor, wherein the stripping gas is chosen from the group of vaporized propylene and ethylene.

On basis of the above process steps, especially wherein the stream from the agitated bed from the reactor is contacted with a stripping gas, one or more aspects are fulfilled. In other words, the step of collecting the polymer particles will result in the formation of a stream of polymer particles having a C4-C8 olefins content that is lower than the C4-C8 olefins content of the stream of polymer particles formed in the agitated bed from the reactor

In an example of the present process, namely after the step of contacting the stream of polymer particles formed in the agitated bed from the reactor with a stripping gas, the C4-C8 olefins content of the stream of polymer particles thus obtained is reduced with at least 20 wt.%, preferably at least 40 wt.%, more preferably 50 wt.%, compared to the C4-C8 olefins content of the stream of polymer particles formed in the agitated bed, .

In an example of the present process the stripping gas is contacted in a counter-current flow with the polymer particles formed in the agitated bed from the reactor.

In an example of the present process the stripping gas is chosen from the group of vaporized propylene and ethylene.

In an example of the present process the temperature during the step of contacting with the stripping gas is in a range of 50 – 70 °C. In case of using a vaporized propylene from the auto-refrigeration unit, its temperature might be as low as -30 °C.

The present invention will now be discussed with reference to the drawings. The drawings are only for illustrative purposes. Well known equipment such as pumps, valves, measuring and control system have been omitted.

Figure 1 shows a process flow diagram of an olefin polymerization process according to the present invention.

Figure 2 shows a diagram of the temperature of the discharge vessel vs the amount of iso-hexane obtained via a computer simulation program.

According to the flowsheet shown in Figure 1 the olefin polymerization process 100 comprises a reactor 6 with an inlet 1 (liquid) and an inlet 4 (vapor). In reactor 6 the reactants form the polymer particles and a mixed stream 10 of polymer particles and vapor is withdrawn from reactor 6. Mixed stream 10 is sent to a product discharge vessel 11 wherein a separation takes place between a stream 12 of polymer particles and a gas stream 13. Stream 20 is a stripping gas. Stream 13 is sent to a multi-stage compressor 14. The resulting compressed stream 17 is contacted with stream 18, i.e. the vapor outlet of reactor 6. The combined stream 19 is sent to a condenser 7 resulting is a cooled stream 8. Part of stream 8 is a purge 3 (liquid) of the recycle loop. The remainder part 9 is recycled to reactor 6. The combination of vapor stream 17 and vapor outlet 18 from reactor 6 is sent to unit 7 resulting in a stream 8 and a stream 4. According to another embodiment (not shown here) vapor stream 17 can bypass unit 7 and is thus directly combined with vapor stream 4. After withdrawing a liquid purge 3 from stream 8 the remainder stream 9 is combined with fresh monomer feed as stream 2 and the resulting stream 1, combined with stream 4, is used as the inlet stream 5 for reactor 6. There is also the option of stream 2 being fed to stream 8 before liquid purge 3, since typical fresh feeds are added to the separator drum. As shown in figure 1 purge 3 is sent to other process units, i.e. there is not direct recycle or return of that purge 3 to the reactor 6. Although Figure 1 shows a single reactor 6, the reactor may comprise several reactors placed in series.

In the polymer discharge from reactor 6, pressure will drop from reactor pressure (15-25 barg) to close to atmospheric (0-1 barg). The expanding gas will transport the reactor powder from reactor 6 to discharge vessel 11, also called as a bag house, usually located above a purge column (not shown). In discharge vessel 11 the powder and gases are separated, where the powder drops to the bottom and is fed with a rotary feeder to a subsequent process (usually a purge column, not shown here). The gases leave through cloth filters at the top of discharge vessel 11 to prevent carry-over of fines to the off-gas compressor 14. The gases are then compressed back to reactor pressure and recycled to condenser 7.

The present inventors found that dissolved monomers require some time to diffuse from the polymer particles to the gas phase, such that the efficiency of

the degassing can be improved by increasing the residence time in discharge vessel 11. Adding a stripping gas 20 will further improve the efficiency of the degassing. However, an inert gas cannot be used since it will be directly recycled to reactor 6 and build-up in the process to unacceptable levels. In order to remove the higher molecular weight monomers the present inventors found that vaporized main monomer, e.g. ethylene or propylene, are used as stripping gas to lower specifically the amount of heavier monomer going to the next step of the process.

In an embodiment of several reactors placed in series (not shown) the process comprises a sequential polymerization process comprising at least two reactors connected in series, wherein said process comprises the steps of preparing the first terpolymer in a first reactor from propylene, ethylene and 1- hexene, and possibly C4 or C8 as additional monomer, using a first set of conditions, - transferring the first terpolymer and unreacted comonomers of the first reactor to a second reactor, - feeding propylene, ethylene and 1 -hexene to the second reactor, preparing the second terpolymer in the second reactor in the presence of the first terpolymer fraction using a second set of conditions to obtain the terpolymer composition, wherein the first and second set of conditions differ in one or more conditions chosen from the group of pressure, temperature, propylene concentration, ethylene concentration, 1 -hexene concentration and hydrogen concentration. Preferably, in such sequential polymerization process, each of the reactors is a gas- phase reactor, more preferably each of the reactors is a horizontal stirred reactor.

Figure 2 shows a diagram of the temperature of the discharge vessel vs the amount of iso-hexane obtained via a computer simulation program. The modelling results have been produced for three different temperatures, i.e. 60, 65 and 75°C in combination with four different process conditions, i.e. a situation with no stripping gas, and situations with a varying gas flow rate at a fixed temperature (500, 900 and 1500 kg/h). In all situations the residence time is 8 mins. In the simulations, an amount of 6.5 wt.% dissolved propylene (based on estimated concentration under reactor conditions) was used, which would be equivalent to 3000 kg/h. The present inventors found that the propylene that is also dissolved, will serve as sort of an in-situ strip gas, and will promote the removal of hexene too, by lowering its partial pressure in the gas phase and increasing the driving force for its diffusion out of the particles. It will take about 300 sec for the degassing to get complete. Temperature

always needs to be below the melting point of the solids, otherwise a lump would form. The pressure is in a range of 0-1 barg.

CLAIMS

1. A process for polymerization of olefins, such as propylene, ethylene and 1 -hexene, in the presence of a catalyst system in a reactor comprising an agitated bed for forming polymer particles, a plurality of liquid feed ports, and a plurality of gas feed ports, wherein the process comprises the steps of:

- recovering a reactor off-gas comprising H_2, olefins from the reactor,

- feeding the reactor off-gas to a condenser to form a gas-liquid mixture,

- feeding the gas-liquid mixture to a separator to obtain a first gas stream comprising H_2, ethylene and propylene and a first liquid stream comprising H_2, ethylene, propylene and 1 -hexene, wherein fresh propylene is further fed to the separator and/or added to the first liquid stream,

- feeding the catalyst system to the reactor through a port arranged on the top side of the reactor,

- feeding a H_2 poor quench liquid comprising propylene a H_2 rich quench liquid comprising H_2, ethylene and propylene and 1 -hexene to the reactor through the liquid feed ports,

- feeding a H_2 poor bottom gas comprising fresh propylene and a H_2 rich bottom gas comprising H_2, ethylene and propylene through the gas feed ports,

- collecting the polymer particles formed in the agitated bed from the reactor,

- feeding fresh ethylene and fresh C4-C8 olefin to the reactor, wherein the step of collecting the polymer particles formed in the agitated bed from the reactor comprises a step of contacting the stream of polymer particles with a stripping gas thereby forming a stream of polymer particles having a C4-C8 olefins content that is lower than the C4-C8 olefins content of the stream of polymer particles formed in the agitated bed from the reactor,

-compressing and recycling the stripping gas to the reactor, wherein the stripping gas is chosen from the group of vaporized propylene and ethylene.

2. A process according to claim 1, wherein after the step of contacting the stream of polymer particles formed in the agitated bed from the reactor with a stripping gas the C4-C8 olefins content of the stream of polymer particles thus obtained is reduced with at least 20 wt.%, preferably at least 40 wt.%, more preferably 50 wt.%, compared

to the C4-C8 olefins content of the stream of polymer particles formed in the agitated bed.

3. A process according to any one or more of the preceding claims, wherein the stripping gas is contacted in a counter-current flow with the polymer particles formed in the agitated bed from the reactor.

4. A process according to any one or more of the preceding claims, wherein the temperature during the step of contacting with the stripping gas is in a range of 50 – 70 °C.

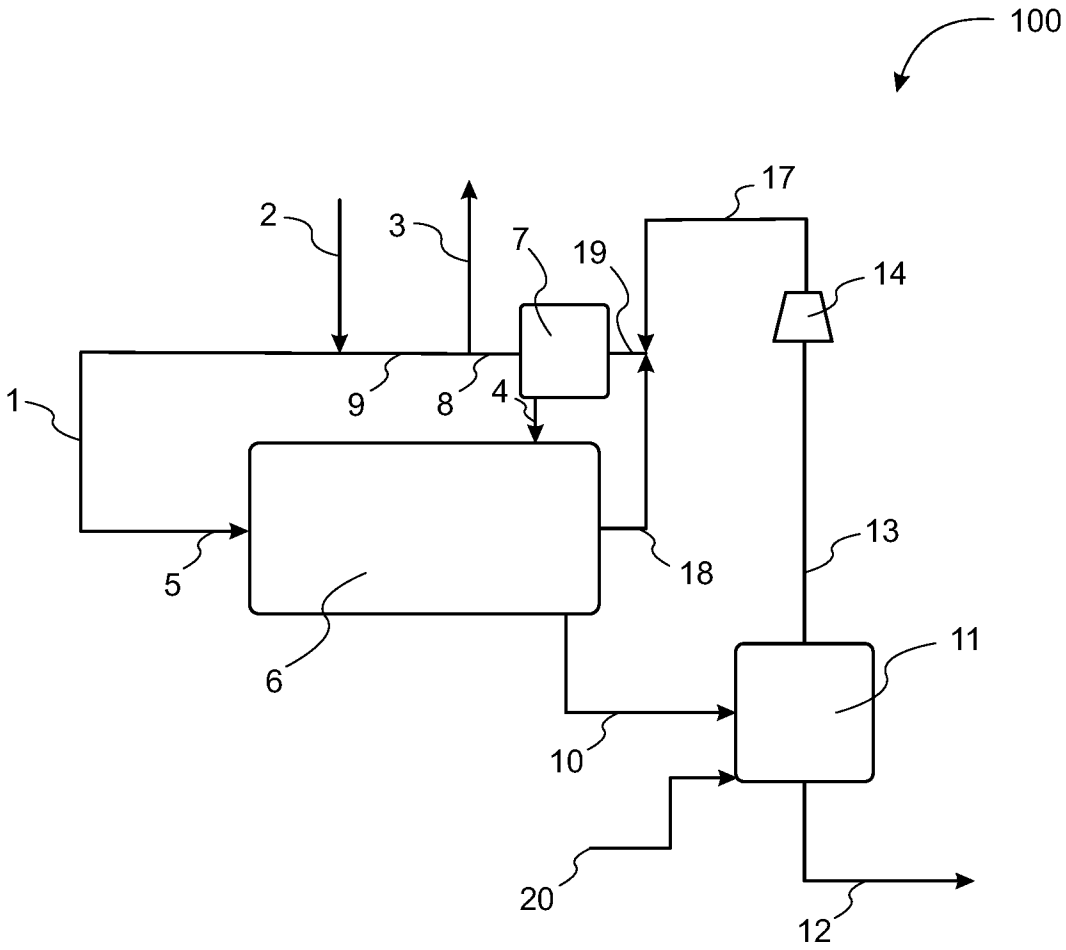


FIG. 1

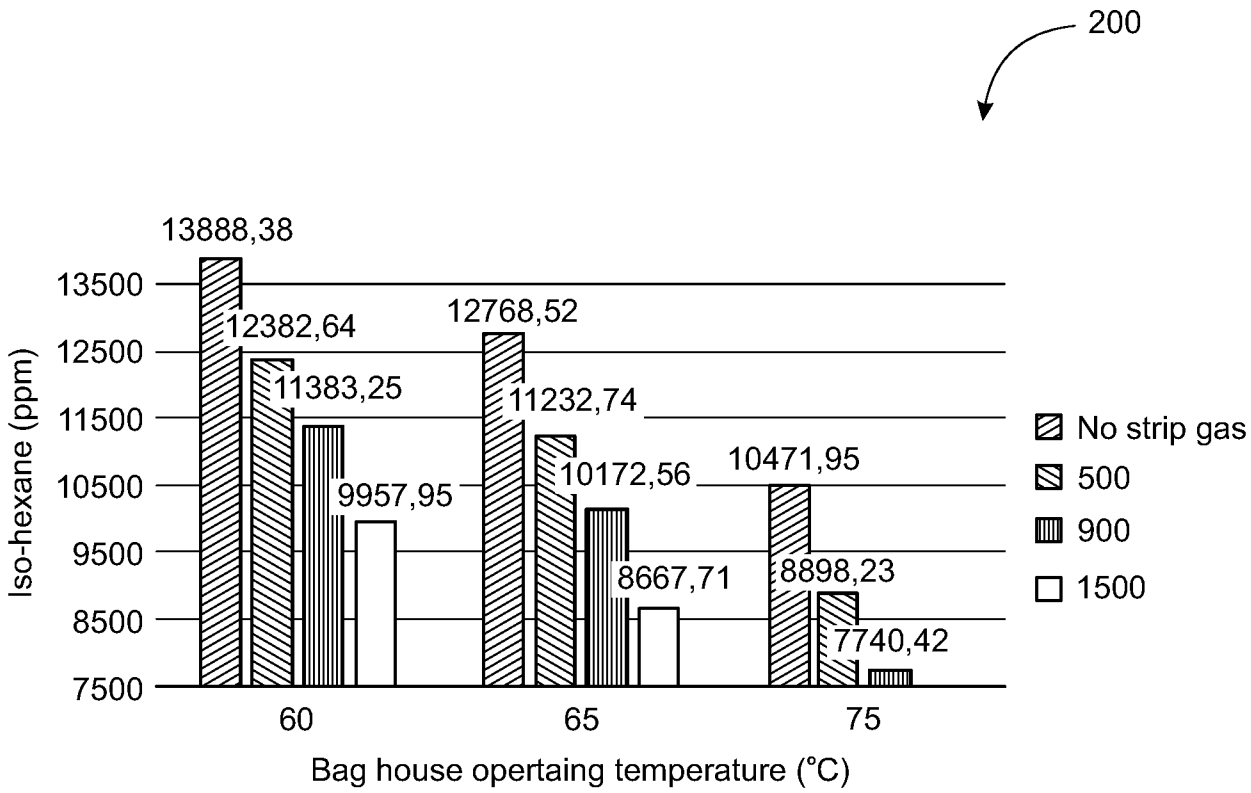

200
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12382,64
11383,25
9957,95
12768,52
11232,74
10172,56
8667,71
10471,95
8898,23
7740,42
13500
12500
11500
10500
9500
8500
7500
Iso-hexane (ppm)
60
65
75
Bag house opertaing temperature (°C)
No strip gas
500
900
1500

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/067214

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F6/00 C08F10/00 C08F2/01 C08F2/34 B01D49/00
B01J8/00 B01J8/08
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F B01J B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 3 438 133 A1 (BASELL POLYOLEFINE GMBH [DE]) 6 February 2019 (2019-02-06) the whole document	1-4
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[x] Further documents are listed in the continuation of Box C.

[x] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 September 2024	17/09/2024

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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