



(51) International Patent Classification:

C03B 3/02 (2006.01) C03B 5/235 (2006.01)

C03B 5/03 (2006.01) C03C 1/00 (2006.01)

C03B 5/225 (2006.01) F23D 99/00 (2010.01)

(21) International Application Number:

PCT/EP2024/064668

(22) International Filing Date:

28 May 2024 (28.05.2024)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

23177878.8 07 June 2023 (07.06.2023) EP

(71) Applicant: AGC GLASS EUROPE [BE/BE]; Avenue

Jean Monnet 4, 1348 Louvain-la-Neuve (BE).

(72) Inventors: **BIOUL, François**; Rue Louis Blériot 12, 6041 Gosselies (BE). **BOURGEOIS, Nicolas**; Rue Louis Blériot 12, 6041 Gosselies (BE). **BOGAERTS, Michel**; Rue Louis Blériot 12, 6041 Gosselies (BE). **HABIBI, Zakaria**; Rue Louis Blériot 12, 6041 Gosselies (BE). **FASILOW, Fabrice**; Rue Louis Blériot 12, 6041 Gosselies (BE).

(74) Agent: **AGC GLASS EUROPE**; Rue Louis Blériot 12, 6041 Gosselies (BE).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO,

(54) Title: GLASS MELTING PROCESS WITH VERY LOW TO ZERO-CO₂ EMISSION

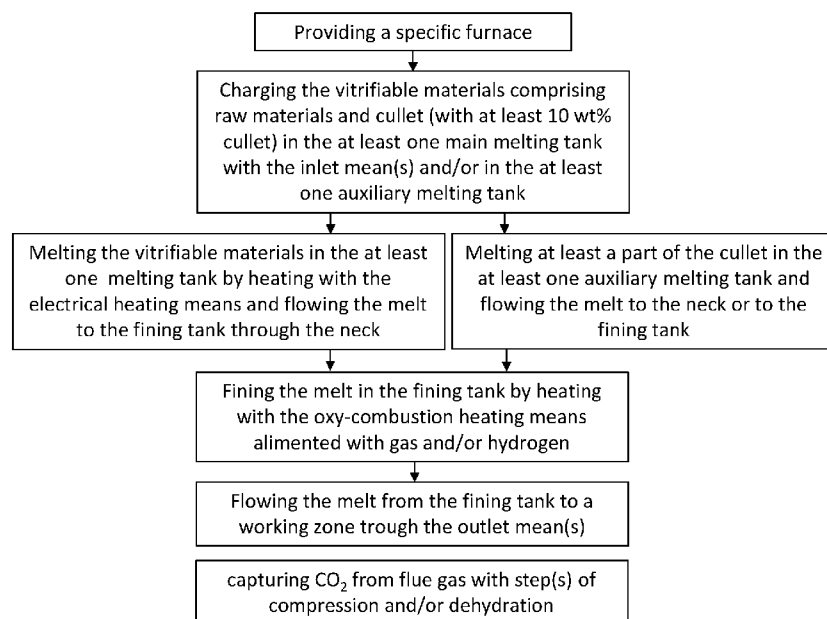


FIG.1

(57) Abstract: The invention concerns a process for melting vitrifiable materials to produce flat glass, comprising the steps of (i) providing a furnace comprising at least one main melting tank with electrical heating means, at least one auxiliary melting tank, a fining tank with oxy-combustion heating means, a neck separating main melting tank and fining tank; (ii) charging the vitrifiable materials comprising raw materials and cullet in main melting tank and/or in auxiliary melting tank, the total amount of cullet being at least 10wt % of vitrifiable materials; (iii) melting the vitrifiable materials in main melting tank by heating with the electrical heating means and flowing to the fining tank through the neck; (iv) melting at least a part of the cullet in the auxiliary melting tank and flowing to the neck or to the fining tank, with electrical input fraction ranging from 50%

RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH,
TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS,
ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to the identity of the inventor (Rule 4.17(i))*
- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *of inventorship (Rule 4.17(iv))*

Published:

- *with international search report (Art. 21(3))*
-

to 85%; (v) fining melt in the fining tank by heating with the oxy-combustion heating means alimented with gas and/or hydrogen, (vi) flowing the melt from the fining tank to a working zone (vii) capturing CO₂ from flue gas comprising step(s) of compression and/or dehydration, said flue gas having CO₂ concentration of at least 35%.

GLASS MELTING PROCESS WITH VERY LOW TO ZERO-CO₂ EMISSION**FIELD OF THE INVENTION**

5 [0001] The present invention relates to a glass melting process aimed at continuously supplying molten glass to flat glass forming installations such as float or rolling installations. In particular, the present invention relates to a glass melting process that provides a lot of advantages, especially in terms of CO₂, especially its emissions and capture.

[0002] The invention is more particularly related, but not limited, to melting process for flat glass
10 involving large production capacities, i.e. up to 1000 tons/day or more.

BACKGROUND OF THE INVENTION

[0003] The global warming and the requirements for CO₂ emissions reduction increase the pressure on glass manufacturers, as well as the energy prices and CO₂ taxes that could become soon a severe
15 threat on competitiveness in the glass sector.

[0004] In that context of urgent action to reduce carbon emissions, the glass industry has invested a lot since years in the decarbonization of its manufacturing processes, with the view to produce glass goods that are fit for a sustainable, resource-efficient, low-carbon society.

[0005] For enabling the transition, the glass sector has already identified a number of
20 solutions/technologies to approach that ambitious goal, as, for example, use of electricity as energy source, use of alternative and greener sources of energy like H₂ or biogas, use of alternative raw materials, increase use of cullet as raw materials, heat recovery, CO₂ capture utilization and storage (or CCUS),...

[0006] Nevertheless, all these technologies are either accompanied by severe drawbacks or issues to
25 practical implementation or are not viable from an economical point of view. There is therefore still an urgent need to have a glass melting process that allows to decrease drastically the amount of CO₂ emitted but while staying economically acceptable for glass manufacturers.

[0007] *As to the use of electricity as source of energy:* it is known that furnace using electrical energy to melt the glass raw materials show a decrease of CO₂ emissions but also a decrease of total energy
30 consumption. In such a configuration, the melting furnace comprises electrodes that allow an electric current/power to pass through and heat the bath of molten glass from its bulk. However, glass melting furnaces where the heating power is entirely supplied by electricity have not been adopted in the flat glass art when a high-quality glass is required, due to serious temperature and glass convection/flow issues.

[0008] Hence, conventional glass melting furnaces for flat glass are generally only “boosted” with electricity, in a so-called “hybrid” configuration combining combustion heating means, namely burners, and electrical heating means, namely immersed electrodes. In such known “electro-boosted combustion furnaces”, the electrical input fraction is nevertheless limited to maximum 10-15% of the total energy input, preventing to fully benefit from the advantages in terms of energy consumption of electrical melting.

[0009] More recently, a new specific design of furnace, described in European patent application EP21200998.9, which are hereby incorporated herein by reference, allows to reach significantly higher electrical input fraction, i.e. above 50%, in an “hybrid” furnace.

[0010] *As to the use of alternative and greener sources of energy like hydrogen H₂ or biogas:* even if it is clear that they will bring advantages in term of environment/energy consumption/CO₂ emissions, serious limitations prevents their extensive use in the glass industry (lack of availability of biogas, and expensiveness of H₂ that makes it a non-economically viable solution so far as the only source of energy to melt glass raw materials).

[0011] *As to heat recovery :* Waste heat recovery from flue gas is already extensively applied in the glass industry to preheat the combustion air entering the furnace at temperatures higher than 1000°C, or gas and oxygen (“Hotox”) at temperatures higher than 400 and 500°C respectively. Next to that, waste heat from flue gas can also be used to preheat the vitrifiable materials, especially cullet. Nevertheless, it is known that pre-heating raw materials/cullet cannot be coupled with electrical melting as the temperature of flue gas released by raw materials in this case is too low.

[0012] *As to the use of CO₂ capture:* Generally, a CO₂ capture process in industrial processes/plants consists of two steps: (i) separation of CO₂ from an effluent gas mixture through a selective reaction with a separation material (“absorption” of CO₂) and (ii) regeneration of the material used by a reverse reaction (“desorption” of CO₂). The separation material can be re-used for CO₂ capture by sequentially repeating steps (i) and (ii). Amines, in the form of solvents or membranes or porous sorbents, are the most widely used material in CO₂ capture process in industry so far, as the technology is mature and an effective separation of amine and CO₂ via a reversible reaction is possible. Nevertheless, such an amine process (e.g., using aqueous MEA) remains a poor option, in particular in the specific context of glass industry so far, at least for the main reasons that :

- the combustion gas/flue gas in known glass manufacturing processes shows a low concentration in CO₂ (generally, below 30% and often around 10-20% in volume) and a low purity due to the presence of a lot of other components (mainly N₂, H₂O, O₂, NO_x, SO_x, etc), thereby affecting greatly the efficiency of the CO₂ capture process; and

- the amine-CO₂ capture process requires a lot of energy in order to regenerate the amine sorbent (desorption process), thereby affecting the total energy consumption (and potentially the CO₂ emission depending of the energy source used, which is obviously counter-productive in present context).

5 [0013] Moreover, known glass manufacturing processes generate very high volumes or flow rates of flue gas, which also directly impacts, whatever the used methods the investment and operational costs when one wants to capture CO₂ from those flue gas.

OBJECTIVE OF THE INVENTION

10 [0014] It is an objective of the present invention to overcome the disadvantages described above with respect to the state of the art and resolving the technical problem, i.e. by providing a glass melting process to produce flat glass, showing a decreased global energy consumption and a decreased CO₂ emissions compared to a classical melting furnace.

[0015] It is a further objective of the present invention to provide a glass melting process to produce
15 flat glass, showing a decreased global energy consumption and a decreased CO₂ emissions compared to a classical melting furnace, that is economically viable.

[0016] It is a further objective of the present invention to provide a glass melting process to produce flat glass, showing a decreased global energy consumption and a decreased CO₂ emissions compared to a classical melting furnace, while allowing a simple and cost-effective CO₂ capture.

20

DESCRIPTION OF THE INVENTION

[0017] The present invention relates to a process for melting vitrifiable materials to produce flat glass, comprising the steps of :

- providing a furnace comprising (i) at least one main melting tank comprising electrical
25 heating means, (ii) at least one auxiliary melting tank, (iii) a fining tank provided with oxy-combustion heating means, (iv) at least one neck separating the at least one main melting tank and the fining tank, (v) inlet mean(s) located at the at least one main melting tank, (vi) outlet mean(s) located downstream of the fining tank;
- charging the vitrifiable materials comprising raw materials and cullet in the at least one
30 main melting tank with the inlet mean(s) and/or in the at least one auxiliary melting tank, the amount of cullet being at least 10% in weight of the total amount of vitrifiable materials;
- melting the vitrifiable materials in the at least one main melting tank by heating with the electrical heating means and flowing the melt to the fining tank through the neck
- melting at least a part of the cullet in the at least one auxiliary melting tank;

- fining the melt in the fining tank by heating with the oxy-combustion heating means alimented with gas and/or hydrogen;
- flowing the melt from the fining tank to a working zone trough the outlet mean(s);
- capturing CO₂ from flue gas, said flue gas having a CO₂ concentration of at least 35%;

5 with its electrical input fraction ranging from 50% to 85%; with the step of capturing CO₂ from flue gas comprising step(s) of compression and/or dehydration; and with a step of flowing the melt from the at least one auxiliary melting tank to the neck or to the fining tank.

[0018] Hence, the invention is based on a novel and inventive approach. In particular, the inventors have found that by combining, in a glass melting process to produce flat glass:

- 10 - the use of a furnace with a specific segmented design (separating an electrically-heated main melting zone and a combustion-heated fining zone),
- the use of oxygen as comburant,
- the use of gas and/or hydrogen as combustible,
- the use of a minimum amount of cullet in the vitrifiable materials,
- 15 - the use of a step of melting cullet, at least partially, in an auxiliary melter that flows downstream of the melting tank (esp. in the neck or in the fining tank), and
- the use of a specific electrical input fraction,

it is possible to obtain, at the same time :

- a significant decrease of the total energy consumption; and
- 20 - a significant decrease of the total CO₂ production; and
- a significant decrease of the volume of flue gas as well as a significant increase of the CO₂ concentration in said flue gas and its purity, thereby allowing to use a simple, efficient and cost-effective CO₂ capture process.

[0019] By implementing all the features of the invention, the process of the invention shows a very
25 low CO₂ fingerprint and is economically viable.

[0020] In present specification and claims, it is well understood by the person skilled in the art that, as used herein the terms "a", "an" or "the" means "at least one" and should not be limited to "only one" unless explicitly indicated to the contrary. Also, when a range is indicated, the extremities are included. In addition, all the integral and subdomain values in the numerical range are expressly
30 included as if explicitly written. Finally, the terms "upstream" and "downstream" refer to the flow direction of the glass and are to be understood with their common sense, namely as meaning along the averaged moving direction of the vitrifiable materials/the glass melt, from the inlet mean(s) to the outlet mean(s). The expression "upstream part" is understood to mean the first upstream third of the

length, said length being located along the horizontal and longitudinal axis of the furnace. The expression “downstream part” is understood to mean the last downstream third of said length.

[0021] Other features and advantages of the invention will be made clearer from reading the following description of preferred embodiments and figure, given by way of simple illustrative and non-restrictive examples.

[0022] FIG. 1 is a flowchart of an embodiment of the process of the invention.

[0023] According to the invention and as illustrated at FIG.1, the process for melting vitrifiable materials to produce flat glass comprises a step of providing a furnace comprising (i) at least one main melting tank comprising electrical heating means, (ii) at least one auxiliary melting tank, (iii) a fining tank provided with oxy-combustion heating means, (iv) at least one neck separating the at least one main melting tank and the fining tank, (v) inlet mean(s) located at the at least one main melting tank, (vi) outlet mean(s) located downstream of the fining tank (for the melted glass to flow to a working zone).

[0024] According to the invention and as commonly adopted in the glass art, by “melting tank”, it is meant a tank defining a zone where the vitrifiable materials (raw materials and/or cullet) are charged and melt by heating, and comprising, when the furnace is in process, a melt and a “blanket” of unmelted vitrifiable materials that floats on the melt and is progressively melted.

[0025] According to the invention and as commonly adopted in the glass art, by “fining tank”, it is meant a tank defining a zone where there is no more “blanket” of unmelted vitrifiable materials that floats on the melt and where the glass melt is heated at temperatures higher than melting tank temperatures (generally above 1400°C or even above 1450°C), in order to refine the glass (mainly by eliminating major part of bubbles). This fining tank is also commonly called “clarification tank” in the art.

[0026] According to the invention, by a “neck” separating the at least one main melting tank and the fining tank, it is meant :

- a narrowing in width compared to the melting tank;
- a narrowing in width and in (crown) height compared to the fining tank; and
- the opening of the neck being only partially under the glass melt/blanket free surface, then leaving a free opening above the glass melt/blanket.

[0027] The crown of the neck according to the invention may be at a lower height than the crown of the main melting tank or essentially at the same height.

[0028] Next to the advantages of the specific furnace design with a neck in combination with the other features of the invention, the neck also allows a wider opening and therefore lower glass velocities leading to lower refractory corrosion and wear. This point can advantageously improve

furnace lifetime. Moreover, it provides a free surface that can be used to control glass temperature flowing out of the neck (important to control convection loops in the fining tank), and to possibly introduce skimbar/barriers introduced from the sides of the neck (can be used to control convection in the neck, and possibly avoid backward flow from fining to melting zone).

5 [0029] Moreover, this furnace design, with a segmentation of the main melting tank(s) and fining tank, brings a lot of advantages in favour of energy consumption/CO₂ emissions and in favour of mechanical stability/ lifetime of the furnace. In particular, advantageously in the context of present invention, this furnace with its specific segmented design allows to deal with flue gas from main melting tank(s) and flue gas from fining tank independently, if desired.

10 [0030] The invention of segmented glass furnace described in European patent application EP21200998.9 and all its embodiments are herein incorporated by reference, as embodiments of the present invention.

[0031] According to a particular embodiment, the furnace of the invention is defined by the following :

15 $0.1 \cdot W2 \leq W3i \leq 0.6 \cdot W2;$
 $W1i \geq 1.4 \cdot W3i;$
W1i being the width of the at least one main melting tank;
W2 being the width of the fining tank;
W3i being the width of the at least one neck.

20 [0032] This last specific design is advantageous to find a good compromise between two opposite requirements : from one side, the neck(s) between the melting zone(s) and the fining zone should be ideally as narrow as possible in order to (1) decrease the opening between melting and fining superstructures/crowns and (2) generate an obstacle to global glass melt convection strength in the main melting tank(s), and, from the other side, the neck should be ideally as wide as possible in order
25 to limit glass velocity inside the neck(s), to limit neck refractory wall wear/corrosion.

[0033] According to the invention, the furnace may comprise one main melting tank and one neck; or two main melting tanks and two necks; or even three main melting tanks and three necks. Embodiments of these specific designs are extensively described in European patent application EP21200998.9 herein incorporated by reference.

30 [0034] For example, in a “two-melting tanks” configuration, the furnace may comprise :

- (i) a first main melting tank,
- (ii) a second main melting tank;
- (iii) a fining tank,
- (iv) a neck Ni separating first main melting tank and the fining tank;

- (v) a neck Nii separating second main melting tank and the fining tank;
- (vi) at least one inlet mean located at the first main melting tank;
- (vii) at least one inlet mean located at the second main melting tank;
- (viii) at least one outlet mean located at the fining tank.

5 [0035] According to this specific embodiment, the furnace may be advantageously defined by the following :

$$0.1*W2 \leq W3i \leq 0.6*W2;$$

$$0.1*W2 \leq W3ii \leq 0.6*W2;$$

$$W1i \geq 1.4*W3i;$$

10 $W1ii \geq 1.4*W3ii;$

W1i being the width of first main melting tank;

W1ii being the width of second main melting tank;

W2 being the width of the fining tank;

W3i being the width of neck Ni;

15 W3ii being the width of neck Nii.

[0036] Preferably, the total surface area of the main melting tank(s) ranges from 25 to 400 m². Preferably also, according to the invention, the surface area of the fining tank ranges from 25 to 400 m².

20 [0037] Preferably, and as known in the art, said inlet mean(s) is/are either located upstream of the at least one melting tank (either in the width of said tank or laterally in its length) or located at the top of the at least one melting tank ("top batch charger").

[0038] In an advantageous embodiment of the invention, the furnace comprises at least one melting tank enlarged laterally and equipped with at least two inlet means, located on both sides of the melting tank based on the location of the neck, either at the lateral sides or as top batch chargers.

25 [0039] According to the invention and as illustrated at FIG.1, the process for melting vitrifiable materials to produce flat glass comprises a step of charging the vitrifiable materials comprising raw materials and cullet in the at least one main melting tank with the inlet mean(s) and/or in the at least one auxiliary melting tank.

30 [0040] According to the invention and as illustrated at FIG.1, the process for melting vitrifiable materials to produce flat glass comprises a step of melting at least a part of the cullet in the at least one auxiliary melting tank and flowing the melt (namely, the melted cullet) to the neck or to the fining tank. For the sake of clarity, this means that the at least one auxiliary melting tank according to the invention is connected (or, in other words, flows) to the neck or to the fining tank.

[0041] Advantageously, the process of the invention comprises a step of melting at least a part of the cullet in the at least one auxiliary melting tank and flowing the melt to the neck. This allows to introduce the molten cullet in a symmetrical way, regarding the complete furnace, leading to better glass homogeneity in the fining tank and in the final glass product.

5 [0042] When the at least one auxiliary melting tank flows (or is connected) to the fining tank, the at least one auxiliary melting tank is preferably connected at the upstream part of the fining tank, and more preferably, as upstream as possible of the fining tank.

[0043] When the at least one auxiliary melting tank flows (or is connected) to the fining tank, this can be done through a connection commonly known in the art, preferably a throat or a neck.

10 [0044] When the at least one auxiliary melting tank flows (or is connected) to the neck, this is preferably done through a connection commonly known in the art, like a throat.

[0045] Alternatively and advantageously, when the at least one auxiliary melting tank flows (or is connected) to the neck, the flowing can be done from a height higher than the top of the neck, the melt coming from the auxiliary melting tank flowing by gravity on the upper surface of the melt already present in the neck (and coming from the main melting tank). This reduces the required space around the neck at the ground level, and make easier operations inside the neck (for equipment introduction for instance). This could also advantageously be combined with a purification process that could be gravity-flow process.

20 [0046] According to an embodiment, the furnace of the invention may comprise more than one auxiliary melting tank, for example, two or three auxiliary melting tanks. In such a case, each auxiliary melting tank may flow/be connected independently to the neck or to fining tank. For example, if the furnace comprises two auxiliary melting tanks, one auxiliary melting tank flows to the neck and the other flows to the fining tank, or both flow to the neck, or both flow to the fining tank. In an alternative embodiment, when the furnace of the invention comprises more than one auxiliary melting tank, for example, two or three auxiliary melting tanks, they may be arranged in series (one after the other). For example, if the furnace comprises three auxiliary melting tanks arranged in series, the first one (the most upstream from the neck or fining tank) flows to the second one that flows to the last one that finally flows to the neck or to the fining tank.

25 [0047] For the sake of clarity, according to the invention, the total amount of cullet charged in the furnace of the invention is either fully and only charged in the at least one auxiliary melting tank (meaning that only raw materials from the vitrifiable materials of the invention are charged in the at least one main melting tank) or, alternatively, the total amount of cullet is split between the at least main melting tank and the at least one auxiliary tank (this means that only a part of the cullet is melted in the at least one auxiliary melting tank, the remaining part of the cullet being melted in the at least

one main melting tank). According to this last embodiment, for example, the part of the cullet that is considered as “polluted” or not sufficiently clean is melted in the at least one auxiliary melting tank and the remaining “clean” part of the cullet is charged, together with raw materials, and melted in the at least one main melting tank.

5 **[0048]** For the sake of clarity also, according to the invention, at least a part of the cullet (namely a part of the total amount of cullet charged in the furnace of the invention) is charged in the at least one auxiliary melting tank, meaning that essentially cullet is charged in the at least one auxiliary melting tank. By “essentially cullet”, it means that cullet is charged alone in the at least one auxiliary melting tank or together with small amounts of compounds (for example, up to 5 or 10 wt% of charged materials), i.e. helping to adjust properties of the melt in the auxiliary melting tank. For example, some soda and/or calcium oxide may be added together with the cullet in order to adjust the viscosity of the melt/melted cullet, without departing from the invention.

[0049] According to an embodiment, if any, the cullet is charged in the at least one main melting tank together with the raw materials, i.e. through same inlet mean(s) or, alternatively, independently of the raw materials through different inlet mean(s).

15 **[0050]** According to an embodiment, the step of melting at least a part of the cullet in the at least one auxiliary melting tank may include one or several steps of purifying said cullet. For example, metallic compounds present in the cullet can be eliminated in this auxiliary melting tank, by using reductants (like coke or anthracite) to produce molten metal that will separate from the glass melt by decanting at the bottom of the auxiliary melting tank, while the obtained “purified” glass melt could flow from the top towards the neck or the fining tank.

20 **[0051]** According to an embodiment of the invention, the at least a part of the cullet that is melted in the at least one auxiliary melting tank represents at least 2% in weight of the total amount of cullet and preferably, at least 5% in weight, or even at least 10% in weight, and more preferably, at least 25 20% in weight.

[0052] According to the invention, the step of melting at least a part of the cullet in the at least one auxiliary melting tank may be carried out with electrical heating means like, for example, immersed electrodes and/or with combustion means like, for example, aerial burners or immersed combustion means.

30 **[0053]** According to the invention, the amount of cullet is at least 10% in weight of the total amount of vitrifiable materials. Preferably, the amount of cullet is at least 20% in weight of the total amount of vitrifiable materials. More preferably, the amount of cullet is at least 30% in weight of the total amount of vitrifiable materials, or even, very preferred, at least 40% in weight. This is advantageous as it allows to reduce the CO₂ production/emission of the process of the invention (due to a reducing

of the emission occurring from the decarbonization of the carbonate raw materials). Possibly, the amount of cullet is at maximum 90% in weight of the total amount of vitrifiable materials, or even at maximum 80% in weight.

[0054] According to the invention and as illustrated at FIG.1, the process for melting vitrifiable materials to produce flat glass comprises a step of melting the vitrifiable materials in the at least one main melting tank by heating with the electrical heating means.

[0055] Electrical heating means according to the invention are possibly located at the bottom of the at least one main melting tank and preferably, in such a case, composed of immersed electrodes. The “bottom electrodes” are advantageously arranged in grid pattern (checkerboard) multiple of 3 or 2, in order to facilitate connection to transformers and electric current balance.

[0056] Alternatively, the electrical heating means according to the invention extends from the top of the at least one main melting tank (for example, maintained commonly by a water-cooled holder) and are immersed. These “top electrodes” are advantageously located along the edge of the melting tank and/or at the corner(s).

[0057] The number of electrodes in the invention is for example designed in order to limit maximum power for each electrode to 400kW, by respecting a maximum current density of $1.5\text{A}/\text{cm}^2$ at the electrode surface. For example, in the case of immersed electrodes, height is between 0.3 and 0.8 times glass melt height.

[0058] According to the invention, the electrical input fraction ranges from 50% to 85%. By “electrical input fraction” according to the invention, it is meant the part of electricity in the total energy input of the process/furnace for the melting/fining, namely $\text{electricity}/(\text{fuel}+\text{electricity})$, the total energy input being that of the process/furnace in standard/normal production mode, i.e. at its standard pull range (excluding periods of start-up, maintenance, hot repair, culleting,...).

[0059] According to the invention and as illustrated at FIG.1, the process for melting vitrifiable materials to produce flat glass comprises a step of fining the melt in the fining tank by heating with the oxy-combustion heating means alimented with gas and/or hydrogen. The term “gas” herein includes, but not only, natural gas, synthetic gas and biogas. Natural gas is the most widely used presently for practical, economical and availability reasons.

[0060] By “oxy-combustion means” according to the invention, it is meant combustion means supplied with gaseous oxygen (O_2) as comburant. Generally, O_2 gas comburant supplied to glass melting furnaces is at least 90% purity, or even at least 95% purity. An advantage of using gaseous oxygen as comburant, compared to using air, is the drastic decrease of the so-called « NO_x » pollutants appearing during the combustion. Even if they could still be present in the flue gas (depending on the O_2 purity and amount of parasitic air), it will be in very low amounts.

[0061] Oxy-combustion heating means according to the invention may be composed of burners, advantageously arranged along the side walls of said tank on each side thereof to spread the flames over practically the entire width of the tank. The burners may be spaced from one another in order to distribute the energy supply over a portion (i.e. ~50% of the length) of the fining tank. They are also commonly arranged in rows on either side of the tank.

[0062] According to the invention, the oxy-combustion heating means are alimented with gas and/or hydrogen. In an embodiment, the oxy-combustion heating means are alimented with at least 50% hydrogen and preferably, at least 80% hydrogen. More preferably, the oxy-combustion heating means are alimented with 100% hydrogen. This is advantageous as it allows to decrease drastically to global CO₂ emission of the process. In an alternative, the oxy-combustion heating means are alimented with more than 50% gas and preferably, at least 80% gas, or even at least 100% gas. This is advantageous as it allows to reach a higher concentration of CO₂ in the flue gas, thereby facilitating and improving the CO₂ capture step, but also to limit impact on the chemistry of glass and on furnace refractory materials. In a specific and advantageous embodiment of the invention, the oxy-combustion heating means are alimented with 50% gas and 50% hydrogen.

[0063] According to the invention and as illustrated at FIG.1, the process for melting vitrifiable materials to produce flat glass comprises a step of flowing the melt from the fining tank to a working zone through the outlet mean(s).

[0064] According to the invention, the outlet mean(s) is/are located downstream of the fining tank, for the melted glass to reach a working zone. According to an embodiment, the outlet mean(s) is/are composed usually of a neck, in order to lead the melt towards a working zone commonly called "working end". Alternatively, the outlet mean(s) is/are composed of a throat, in order to lead the melt towards a working zone including, for example, forehearth(s). The working zone according to the invention may comprise, for example, a conditioning zone in which thermal conditioning by controlled cooling is carried out prior to glass melt leaving said zone through an outlet to a forming zone. Such a forming zone may comprise, for example, a float installation and/or a rolling installation.

[0065] According to another advantageous embodiment, the furnace of the invention may comprise a removable wall located at the neck (e.g. a skimbar coming from the side wall of the neck), in order to (i) possibly stop unmelted vitrifiable materials that could arrive at the end of the melting tank and thereby avoid their passing through the neck towards the fining tank and (ii) control the intensity of or annihilate the backward flow of the melt from the fining towards the melting tank.

[0066] According to still another advantageous embodiment of the invention, the furnace may comprise a removable wall located at the neck (e.g. a shadow wall passing through the crown of the

neck) in order to increase segmentation of melting and fining tanks in terms of atmosphere and heat radiations.

[0067] According to the invention and as illustrated at FIG.1, the process for melting vitrifiable materials to produce flat glass comprises further a step of capturing CO₂ from flue gas.

5 **[0068]** According to the invention, said flue gas (namely the flue gas which undergoes the step of CO₂ capture) has a CO₂ concentration of at least 35%. The CO₂ concentration according to the invention is the concentration defined for the dry flue gas, namely the flue gas with all its components except the water (H₂O). Preferably, the flue gas in the invention has a CO₂ concentration of at least 40%, and more preferably, of at least 50%, or even more of at least 60%. This is advantageous as the higher the
10 concentration in CO₂ of the flue gas, the easier and effective the CO₂ capture applied on this flue gas.

[0069] According to the invention and as illustrated at FIG.1, the step of capturing CO₂ from flue gas comprises step(s) of compression and/or dehydration. The step of dehydration corresponds to a step of water condensation and/or drying of the flue gas. The step of compression corresponds to increasing the pressure of CO₂, commonly by using a compressor. The step of dehydration may be
15 prior to the step of compression, and/or the step of dehydration may be concomitant to the step of compression.

[0070] In particular, the step of capturing CO₂ from flue gas according to the invention may be carried out, in a known manner, using a CO₂ compression and purification unit (or CPU).

[0071] The flue gas according to this invention may be recovered for CO₂ capture either from (i) the
20 at least one main melting tank, (ii) from the at least one main melting tank and the at least one auxiliary melting tank, (iii) from the fining tank or (iv) from the whole furnace. In particular, if the oxy-combustion heating means according to the invention are alimented with hydrogen only, the flue gas are advantageously recovered only from the at least one melting tank (the flue gas evolving from the fining tank does not include CO₂) or from the at least one main melting tank and the at least one
25 auxiliary melting tank.

[0072] After the step of capturing CO₂ according to the invention, the CO₂ product has, for example, a pressure of about 35 bar at temperature 5°C-40°C, in a gaseous form, appropriate for transport through pipelines, or of about 100 bar in the liquid form, appropriate for transport through pipelines but also truck or rail transport. For transport by truck, a value of 15 bar at -35°C is also known as
30 appropriate.

[0073] This simple and effective CO₂ capture process is very advantageous as it allows avoiding the use of any sorbent/chemical reagents that would contribute to operating/energy costs and environmental issues, and as it allows to reach a CO₂ capture that is cost-effective, rendering the whole process of the invention economically viable.

[0074] According to a preferred embodiment, the step of capturing CO₂ from flue gas consists essentially in step(s) of compression and/or dehydration.

[0075] According to an advantageous embodiment, the process of the invention comprises further a step of eliminating acidic components from flue gas. This step of eliminating acidic components is carried out prior or concurrent to the step of capturing CO₂ (for example prior to or concurrent to/together with the step(s) of compression and/or dehydration).

[0076] The step of eliminating acidic components may include a step of desulphurization (or removing of the so-called « SO_x » compounds) of the flue gas. It may also include a step of removing the so-called « NO_x » compounds, that could still be present even if in very low amounts due to the use of oxygen as comburant. This is advantageous as this allows removing the corrosive compounds (SO_x, NO_x) before the transportation, storage and/or utilization.

[0077] After the step of capturing CO₂ according to the invention, in a known manner, the CO₂ product (for example, in a liquid form) may be transported to its final destination through pipelines, then either stored/sequestered (for example, deep undersea or in a geological formation such as a saline aquifer) or, alternatively, utilized (for example, for enhanced oil recovery, or for food/beverage applications or for fire protection applications). Advantageously, the CO₂ product obtained after the step of capturing CO₂ may be used locally, to limit transportation. This can be considered if the amount of CO₂ captured is not too high so that it can be absorbed by local market(s).

[0078] According to an advantageous embodiment of the invention, the process comprises further a step of cullet pre-heating, at least partially by recovering heat from the furnace, before charging said cullet in the at least one main melting tank and/or in the at least one auxiliary melting tank. According to this embodiment, recovering heat from the furnace may be carried out from flue gas coming from (i) the melting tank(s), or (ii) the fining tank or (iii) from the whole furnace (thereby including flue gas from the melting, auxiliary and/or main one(s), and fining tanks).

[0079] According to this embodiment and advantageously, the CO₂ capturing step may be carried out from the flue gas that is used at the step of cullet pre-heating.

[0080] According to this embodiment also, if only a part of the cullet is melted at the step of melting in the auxiliary melting tank and if the remaining part of the cullet (to be charged in the main melting tank) is pre-heated, the raw materials are charged in the at least one main melting tank either together with the pre-heated cullet through same inlet mean(s) (this implies therefore that both type of vitrifiable materials are mixed before charging) or independently of the pre-heated cullet, through different inlet mean(s).

[0081] Preferably, according to this embodiment, the maximum temperature of the cullet at the step of cullet pre-heating is 450°C. This allows to avoid clogging issues.

[0082] According to an embodiment, the step of cullet pre-heating may be carried out in at least one cullet pre-heater, for example, of the type of one of those described in US5526580 or DE3716687.

[0083] Advantageously, the at least one cullet pre-heater may be located at upstream part of the at least one main melting tank or of the at least one auxiliary melting tank, either in the width of said tank or laterally in its length. Advantageously and in particular for the at least one main melting tank, the step of cullet pre-heating may be carried out in at least two cullet pre-heaters located, for example, at upstream part of the main melting tank, in its width or laterally in its length on both sides. For example, the step of cullet pre-heating may be carried out in four cullet pre-heaters located at upstream part of the main melting tank, distributed in its width or laterally in its length (for example, two on each side). For example also, the step of cullet pre-heating may be carried out in six cullet pre-heaters located at upstream part of the main melting tank, in its width or laterally in its length (for example, three on each side), or also in eight cullet pre-heaters located at upstream part of the main melting tank, in its width or laterally in its length (for example, four on each side).

[0084] According to still another advantageous embodiment of the invention, the raw materials comprise less than 25% in weight of carbonate compounds. By "carbonate compounds", it is meant for example alkali carbonates and alkaline earth carbonates. Preferably, the raw materials comprise less than 20% in weight of carbonate compounds, and more preferably less than 10%, and even less than 5%. The raw materials may be advantageously free of any carbonate compound.

[0085] This embodiment is advantageous as it allows to reduce the part of CO₂ emission occurring from the decarbonization of raw materials, compared to classical glass melting process where sodium carbonate Na₂CO₃, limestone CaCO₃ and dolomite CaMg(CO₃)₂ are generally essentially used as sources of sodium and calcium. According to this embodiment, the alkali and alkaline earth sources may advantageously be present, at least partially, in the form of oxides or hydroxides such as CaO, CaO.MgO (dolime), Ca(OH)₂, Mg(OH)₂, NaOH, KOH.

[0086] According to a very preferred embodiment of the invention, the process for melting vitrifiable materials to produce flat glass comprises the steps of :

- providing a furnace comprising (i) at least one main melting tank comprising electrical heating means, (ii) at least one auxiliary melting tank, (iii) a fining tank provided with oxy-combustion heating means, (iv) at least one neck separating the at least one main melting tank and the fining tank, (v) inlet mean(s) located at the at least one main melting tank, (vi) outlet mean(s) located downstream of the fining tank;
- charging the vitrifiable materials in the at least one main melting tank with the inlet mean(s) and/or in the at least one auxiliary melting tank, said vitrifiable materials comprising (i) raw

materials with less than 25% in weight of carbonate compounds and (ii) cullet in an amount of at least 10% in weight of the total amount of vitrifiable materials,

- cullet pre-heating, at least partially by recovering heat from the furnace, before charging said cullet in the at least one main melting tank and/or the at least one auxiliary melting tank;
- melting the vitrifiable materials in the at least one main melting tank by heating with the electrical heating means and flowing the melt to the fining tank through the neck, the electrical input fraction of the process ranging from 50% to 85%;
- melting at least a part of the cullet in the at least one auxiliary melting tank and flowing the melt to the neck or to the fining tank;
- fining the melt in the fining tank by heating with the oxy-combustion heating means alimented with gas and/or hydrogen;
- flowing the melt from the fining tank to a working zone through the outlet mean(s);
- capturing CO₂ from flue gas having a CO₂ concentration higher than 35%, this step comprising step(s) of compression and/or dehydration.

[0087] All previously described specific embodiments related to each step of the process of the invention applies to this last very preferred embodiment.

[0088] The person skilled in the art realizes that the present invention is by no means limited to the preferred embodiments described above. On the contrary, many modifications and variations are possible within the scope of the appended claims. It is further noted that the invention relates to all possible combinations of features, and preferred features, described herein and recited in the claims.

CLAIMS

1. Process for melting vitrifiable materials to produce flat glass, comprising the steps of :
 - 5 - providing a furnace comprising (i) at least one main melting tank comprising electrical heating means, (ii) at least one auxiliary melting tank, (iii) a fining tank provided with oxy-combustion heating means, (iv) at least one neck separating the at least one main melting tank and the fining tank, (v) inlet mean(s) located at the at least one main melting tank, (vi) outlet mean(s) located downstream of the fining tank;
 - 10 - charging the vitrifiable materials comprising raw materials and cullet in the at least one main melting tank with the inlet mean(s) and/or in the at least one auxiliary melting tank, the amount of cullet being at least 10% in weight of the total amount of vitrifiable materials;
 - melting the vitrifiable materials in the at least one main melting tank by heating with the electrical heating means and flowing the melt to the fining tank through the neck
 - 15 - melting at least a part of the cullet in the at least one auxiliary melting tank;
 - fining the melt in the fining tank by heating with the oxy-combustion heating means alimented with gas and/or hydrogen;
 - flowing the melt from the fining tank to a working zone trough the outlet mean(s);
 - capturing CO₂ from flue gas, said flue gas having a CO₂ concentration of at least 35%;
 - 20 characterized in that :
 - its electrical input fraction ranges from 50% to 85%;
 - the step of capturing CO₂ from flue gas comprises step(s) of compression and/or dehydration;
 - it comprises a step of flowing the melt from the at least one auxiliary melting tank to the
 - 25 neck or to the fining tank.
2. Process for melting vitrifiable materials according to preceding claim, characterized in that the amount of cullet is at least 30% in weight of the total amount of vitrifiable materials.
3. Process for melting vitrifiable materials according to preceding claims, characterized in that the oxy-combustion heating means are alimented with at least 50% hydrogen and preferably, at least
30 80% hydrogen.
4. Process for melting vitrifiable materials according to preceding claims, characterized in that said flue gas has a CO₂ concentration of at least 40%.
5. Process for melting vitrifiable materials according to preceding claim, characterized in that said flue gas has a CO₂ concentration of at least 50%.

6. Process for melting vitrifiable materials according to preceding claims, characterized in that the step of capturing CO₂ from flue gas consists essentially in step(s) of compression and/or dehydration.

7. Process for melting vitrifiable materials according to preceding claims, characterized in that it comprises further a step of eliminating acidic components from said flue gas.

8. Process for melting vitrifiable materials according to preceding claim, characterized in that the step of eliminating acidic components from said flue gas is prior or concurrent to the step of capturing CO₂.

9. Process for melting vitrifiable materials according to preceding claims, characterized in that it comprises further a step of cullet pre-heating, at least partially by recovering heat from the furnace, before charging said cullet in the at least one main melting tank and/or in the at least one auxiliary melting tank.

10. Process for melting vitrifiable materials according to preceding claim, characterized in that the maximum temperature of cullet at the step of cullet pre-heating is 450°C.

11. Process for melting vitrifiable materials according to preceding claims, characterized in that the raw materials comprise less than 25% in weight of carbonate compounds.

12. Furnace for carrying out the process of claims 1-11.

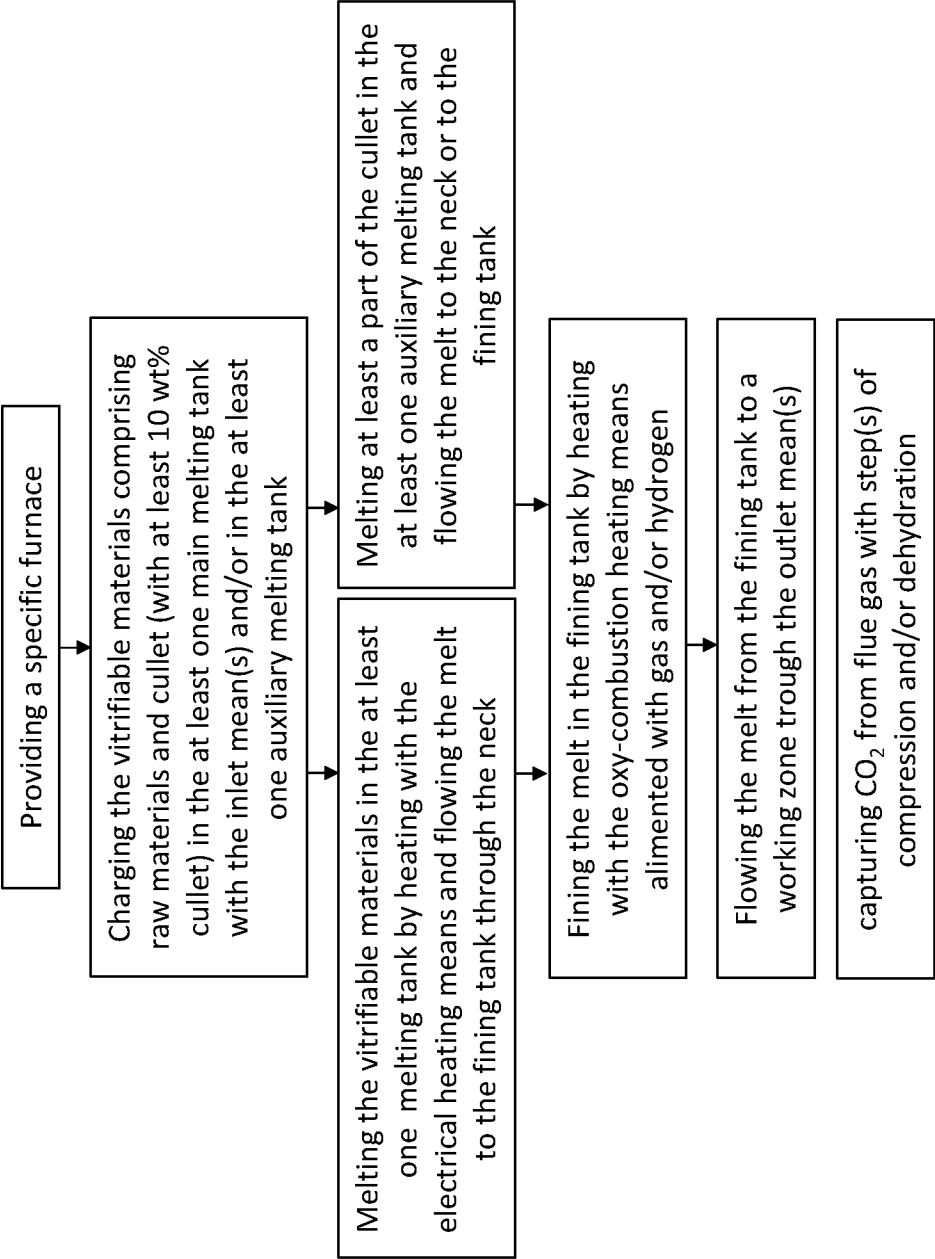


FIG.1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/064668

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C03B3/02	C03B5/03
	F23D99/00	
ADD.	C03B5/225	C03B5/235
		C03C1/00
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)		
C03B C03C F23D F23J		
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.
A	US 2004/168474 A1 (JEANVOINE PIERRE [FR] ET AL) 2 September 2004 (2004-09-02) paragraphs [0092], [0029] - [0030], [0041] - [0042], [0024], [0025]; figure 1	1 - 12
A	JP JP7 153 241 B2 (NIPPON ELECTRIC GLASS CO) 14 October 2022 (2022-10-14) paragraphs [0077], [0102], [0081], [0085]; figure 2	1 - 12
A	WO 2018/039398 A1 (CORNING INC [US]) 1 March 2018 (2018-03-01) paragraphs [0057], [0061]	1 - 12
	- / - -	
☒ Further documents are listed in the continuation of Box C. ☒ 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	"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	
"E" earlier application or patent but published on or after the international filing date	"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	
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"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	
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search	Date of mailing of the international search report	
17 July 2024	08/08/2024	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Gkerou, Elisavet	

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/064668

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 104 418 484 A (XING YUNTAO; XING YISONG; XING YUNJING) 18 March 2015 (2015-03-18) the whole document -----	1 - 12
A	EP 0 761 287 A2 (BOC GROUP INC [US]) 12 March 1997 (1997-03-12) the whole document -----	1 - 12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2024/064668

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2004168474 A1	02-09-2004	AT E397569 T1	15-06-2008
		AU 2004218197 A1	16-09-2004
		BR PI0407828 A	14-02-2006
		CN 1777563 A	24-05-2006
		EP 1599423 A1	30-11-2005
		ES 2308153 T3	01-12-2008
		FR 2851767 A1	03-09-2004
		JP 2007526863 A	20-09-2007
		KR 20050101224 A	20-10-2005
		PT 1599423 E	11-09-2008
		US 2004168474 A1	02-09-2004
		US 2004224833 A1	11-11-2004
		US 2007212546 A1	13-09-2007
		WO 2004078664 A1	16-09-2004

JP JP7153241 B2	14-10-2022	CN 111051255 A	21-04-2020
		JP 7153241 B2	14-10-2022
		JP WO2019049768 A1	01-10-2020
		KR 20200049778 A	08-05-2020
		TW 201920025 A	01-06-2019
		TW 202231589 A	16-08-2022
		US 2020199012 A1	25-06-2020
		WO 2019049768 A1	14-03-2019

WO 2018039398 A1	01-03-2018	CN 109641771 A	16-04-2019
		EP 3504165 A1	03-07-2019
		EP 3896037 A1	20-10-2021
		JP 7058641 B2	22-04-2022
		JP 2019524630 A	05-09-2019
		KR 20190049756 A	09-05-2019
		KR 20220066433 A	24-05-2022
		TW 201811710 A	01-04-2018
		TW 202214539 A	16-04-2022
		US 2020180990 A1	11-06-2020
		WO 2018039398 A1	01-03-2018

CN 104418484 A	18-03-2015	NONE	

EP 0761287 A2	12-03-1997	AU 711644 B2	21-10-1999
		CA 2181328 A1	24-02-1997
		CN 1152547 A	25-06-1997
		EP 0761287 A2	12-03-1997
		JP H09118529 A	06-05-1997
		KR 970009873 A	27-03-1997
		MY 112986 A	31-10-2001
		NZ 299103 A	26-08-1998
		PL 315804 A1	03-03-1997
		TR 199600676 A2	21-03-1997
		TR 199700937 A1	21-11-2000
		US 5743929 A	28-04-1998
		US 5925326 A	20-07-1999
		ZA 966433 B	19-02-1997
