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EUROPEAN PATENT APPLICATION

21 Application number: 82305965.4

51 Int. Cl.³: **C 22 B 21/06**
F 27 D 23/04

22 Date of filing: 09.11.82

43 Date of publication of application:
16.05.84 Bulletin 84/20

84 Designated Contracting States:
CH DE FR GB LI

71 Applicant: **ALCAN INTERNATIONAL LIMITED**
1188 Sherbrook Street West
Montreal Quebec H3A 3G2(CA)

72 Inventor: **Dubé, Ghyslain**
1663 Gay Lussac
Arvida Quebec(CA)

74 Representative: **Hewlett, Arthur James et al,**
STEVENS, HEWLETT & PERKINS 5 Quality Court
Chancery Lane
London WC2A 1HZ(GB)

54 **Removal of alkali metals and alkaline earth metals from molten aluminium.**

57 For removing contaminant alkali- and alkaline earth metal contaminants, particularly Li, a particulate aluminium fluoride-containing material is introduced into a vortex established in a non-cylindrical body of molten aluminium contained in a vessel.

The generation of the vortex establishes currents having both downward and lateral components at the bottom of the vortex and upwardly spiralling currents at the periphery of the vessel, which serve to recirculate suspended matter.

The stirring of the molten metal is continued until the contaminant level is reduced to a desired level and then the molten Al is separated from the reaction products.

The body of metal is contained in a vessel which is non-cylindrical and/or has its axis inclined to the vertical.

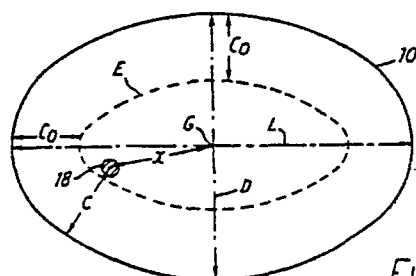


FIG. 1

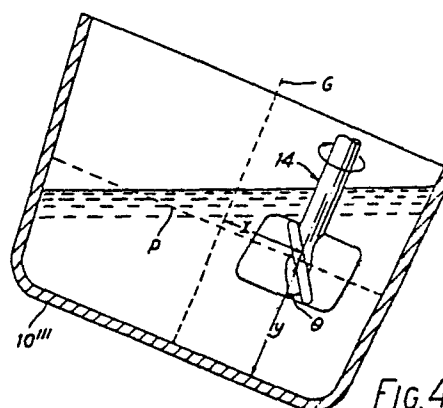


FIG. 4

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"REMOVAL OF ALKALI METALS AND ALKALINE
EARTH METALS FROM MOLTEN ALUMINIUM"

This invention relates to the removal of contaminant quantities of alkali metals and alkaline earth metals from molten aluminium by reaction with aluminium fluoride.

5 A method of treating molten aluminium with a particulate aluminium fluoride-yielding material has been described in our European Patent Application No. 82.302448.4. In that method a charge of contaminated metal is placed in a vessel, in which it is stirred to establish a vortex and flow currents having both downward and lateral components at the bottom of the vortex and
10 upwardly spiralling currents at the periphery of the vessel. The particulate aluminium fluoride-yielding material is supplied to enter the vortex and become entrained in the molten aluminium and the stirring of the molten aluminium is continued until the alkali metal and
15 alkaline earth metal content is reduced to a desired low level.

The vortex was preferably generated by means of a multi-blade impeller having blades inclined to its
20 axis of rotation and in the already described process this was preferably arranged somewhat eccentrically in relation to the axis of a cylindrical vessel having a vertically arranged axis. It was found that optimum results were achieved by careful dimensioning of the
25 impeller in relation to the dimension of the treatment vessel and also to the depth of molten metal to be contained in the vessel, generally a vessel for transferring a body of molten metal from a reduction cell to a casting station.

30 The preferred relationships were established as follows :

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	<u>Relationship or dimension</u>	<u>Outside range</u>	<u>Preferred Range</u>
	d/D	0.1 - 0.6	0.15 - 0.40
	h/H	0.1 - 0.7	0.2 - 0.40
5	y	0.25H - 0.75H	0.4H - 0.6H
	θ	$0^\circ - 45^\circ$	$30^\circ - 40^\circ$

In the above θ designates the pitch angle of the impeller blades, d is the overall diameter of the bladed portion of the impeller, h is the height of the impeller blades, y is the vertical distance from the bottom of the crucible interior to the midpoint of the impeller blades, H is the vertical distance from the bottom of the crucible interior to the quiescent level of molten metal in the crucible, D is the internal diameter of the crucible. The impeller was preferably eccentrically located at a distance of 0.1 - 0.25D and more preferably at a distance of 0.25 - 0.7 d in relation to the axis of the vessel.

In the method, as described in our said European Patent Application No. 82,302448.4 the vortex is generated by a stirrer in a mass of molten metal, which is essentially cylindrical in the unstirred condition. It has now been found that the process can be effectively performed on bodies of molten metal which are initially non-cylindrical (in the non-stirred condition). Solid particulate material can be entrained in and reacted with alkali metal contaminants in molten aluminium by generation of a vortex in such non-cylindrical masses with similar efficiency to that achieved when the metal is contained in an upright cylindrical crucible, thus permitting the process to be employed in all forms of transfer crucible, particularly crucibles having an essentially continuous, rounded sidewall surface free from recesses or abrupt angles, which would result in locally stagnant zones within the upwardly spiralling

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molten metal flow in the peripheral region of the vessel.

Referring now to the accompanying drawings

Figure 1 is a diagrammatic plan view of a crucible having an elliptical cross-section.

Figure 2 is a similar view of a crucible having parallel sides and semi-circular ends.

Figure 3 is a view of a crucible having a downwardly tapering interior arranged at a substantial tilt angle in relation to the vertical, with a stirrer rotating about a vertical axis.

Figure 4 is a similar view to Figure 3, but with the stirrer rotating about an axis parallel to the crucible axis.

In performing the process of the present invention in the crucibles illustrated in Figures 1 - 4 the stirrer is constructed and arranged to operate in the same way as in our co-pending European Patent Application No. 82.302448.4. The stirrer is supported by a lid (not shown) and a duct is arranged on the lid for the supply of a particulate aluminium fluoride-yielding material (which expression embraces compounds such as KAlF_4) on to the surface of the molten metal in the vessel.

During the treatment of molten aluminium with AlF_3 powder, alkali and alkaline earth metals react preferentially with AlF_3 (compared to aluminium) to form mixed alkali cryolithionite compounds, e.g. $\text{Na}_5\text{Al}_3\text{F}_{14}$, $\text{Na}_2\text{LiAlF}_6$, and $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$. These compounds, having a relatively low melting point (compared with pure cryolite), can easily be agglomerated or stick to the crucible walls or float to the melt surface where they react with metal oxide or particles of electrolyte always present after the siphoning of electrolytic cells. During subsequent metal transfer from the crucible by

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siphoning, most of these compounds will remain inside the crucible.

As previously stated, according to the present invention, it is possible effectively to treat contaminated molten Al metal with solid particulate AlF_3 and maintained in a non-cylindrical mass by a crucible or metal-confining vessel with a configuration other than cylindrical and/or an orientation other than vertical. For example, the vessel may be shaped as shown in Figures 1, 2 and 3, and may be axially tilted with even an axially tilted stirrer (Fig. 4), although a vertical axis of stirrer rotation is preferred because of the effect of gravity on vortex generation.

We have found that the preferred dimensional and positional relationships already stated for an upright cylindrical vessel can be more broadly defined with reference to the geometric axis of the vessel, the axis of impeller rotation, and the plane of impeller rotation (viz. the plane, containing the midpoint of the impeller blades, perpendicular to the axis of impeller rotation). Thus, the diameter $\underline{D}$ is the minimum internal diametrical dimension (i.e. measured through the geometric axis of the vessel) of the metal-containing vessel in the plane of impeller rotation. Blade diameter $\underline{d}$ and eccentricity $\underline{x}$ are also measured in the plane of impeller rotation, while blade height $\underline{h}$, distance $\underline{y}$, and distance $\underline{H}$ are all measured along the axis of impeller rotation, and pitch angle θ is measured with reference to the axis of impeller rotation.

With the foregoing definitions, all the relationships and ranges of values (i.e. d/D , h/H , etc.) already given, hold true, except for the outside range of eccentricity $\underline{x}$. In general, the eccentricity is limited only by the requirement that the minimum distance $\underline{C}$ from the axis of impeller rotation to the internal wall of the crucible vessel (again measured in the plane

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of impeller rotation) is at least equal to $D/4$.

Figure 1 represents the cross-sectional configuration (in the plane of impeller rotation) of a crucible or vessel 10' having an elliptical cross-section containing an axially vertical impeller, or of the surface of a body of molten metal contained in a cylindrical crucible tilted with respect to the impeller axis.

In Figure 1 $\underline{G}$ is the geometric axis of the elliptical crucible, $\underline{D}$ is the short diameter of the elliptical cross-section, and $\underline{L}$ is the long diameter of the elliptical cross-section. The axis of impeller rotation can intersect the plane of impeller rotation (viz: the plane of the drawing) anywhere within the area enclosed by broken-line ellipse $\underline{E}$ which is spaced inwardly from the crucible wall by a constant distance $\underline{C}_0 = D/4$.

In the illustrated eccentric position of the impeller shaft 18, the eccentricity $\underline{x}$ is clearly greater than $D/4$, but the axis of impeller rotation is spaced from the crucible wall by a distance $\underline{C}$ greater than $D/4$.

In Figure 2, the cross-sectional configuration of the crucible 10" in the plane of impeller rotation is bathtub-shaped, having semicircular ends and straight parallel sides spaced apart by a distance equal to the diameter of the semi-circular ends. The minimum diameter $\underline{D}$ through the geometric axis $\underline{G}$ in this plane is the distance between the parallel sides (viz. the diameter of the semi-circular ends), while the long diameter $\underline{L}$ is equal to $A + D$, where $\underline{A}$ is the spacing between the centres of the semi-circles. The broken line $\underline{E}$, defining the outer limit of eccentricity of the axis of impeller rotation, is again spaced inwardly from the crucible wall by a constant distance $\underline{C}_0 = D/4$. The impeller shaft 18 is shown in an illustrative eccentric position within this outer limit, having an eccentricity $\underline{x}$.

The crucible 10''' shown in elevational cross-section in Figures 3 and 4 has a geometric axis G tilted with respect to the vertical. In Figure 3 the axis of rotation of the impeller 14 is vertical; hence y is a vertical distance (from the midpoint of the impeller blades to the point on the crucible floor vertically beneath that midpoint) and eccentricity x is measured in the horizontal plane P of impeller rotation, which is at an oblique angle to G. In Figure 4, the axis of rotation of the impeller 14 is tilted to the vertical so as to be parallel to G; y is again measured along the impeller axis, now at an oblique angle to the vertical, and x is measured in rotational plane P which is perpendicular to G but at an oblique angle to the horizontal. The pitch angle θ , as indicated, is in each case measured with reference to the axis of impeller rotation. In both Figures 3 and 4 the crucible 10''' tapers so that its cross-sectional diametrical dimensions decrease in a downward direction; the value of diameter D which determines the various aforementioned dimensional relationships is, in each instance, measured in the plane P.

These different arrangements permitted the removal of Li contamination from Al metal, withdrawn from electrolytic reduction cells, to be achieved within reasonable time, but not in all cases with the same process time as could be achieved with a stirrer eccentrically related to the axis of an upright vertical vessel.

It will be appreciated that a mass of molten metal, held in a tilted cylindrical crucible, assumes an essentially non-cylindrical shape, having an elliptical surface. The top surface of the body of metal in the tilted, tapering crucible of Figures 3 and 4 is also ellipsoidal in shape.

We have found that a vortex can be generated satisfactorily where the impeller is tilted by an angle of up to 15° to the vertical, but with decreasing efficiency as the tilt angle is increased. It is however

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preferred that the tilt angle of the impeller should not exceed about 10° to the vertical. The tilting of the axis of the crucible is of less importance. However, increase of the tilt angle of the crucible will decrease its molten metal-holding capacity. In all cases however improved results are obtained when the crucible (of whatever shape) is maintained in an upright condition.

It should be noted that the treatment material may comprise aluminium fluoride, possibly containing up to 50% inert material, such as aluminium oxide. Alternatively aluminium fluoride may be added in chemically-bound form, such as a fluoaluminate of sodium or potassium. Conveniently it may be added as NaF/AlF_3 having a low NaF/AlF_3 ratio by weight, for example 0.6 - 0.7/1.

Aluminium fluoride may also be added admixed with other alkali metal fluorides or chlorides or alkaline earth metal fluorides or chlorides. As an alternative to aluminium fluoride, any active fluorine-containing compound could be added, i.e. any such compound which on addition to molten aluminium will liberate a fluoride which is reactive towards alkali or alkaline earth metal contaminants and does not introduce other undesirable contaminants into the molten aluminium. KBF_4 and K_2TlF_6 are examples of such compounds.

All such materials are for convenience in the appended claims considered as being embraced by the terms "aluminium fluoride" or "aluminium fluoride-yielding material".

1. A method of removing contaminant alkali metals and alkaline earth metals from a non-cylindrical mass of molten aluminium contained within a vessel by reaction with aluminium fluoride to form fluoaluminates of such contaminants which comprises

(1) stirring said mass of molten aluminium in said vessel under conditions to establish a vortex therein and flow currents in said molten aluminium having both downward and lateral components at the bottom of said vortex and upwardly spiralling currents in the region of the periphery of said vessel

(2) supplying particulate aluminium-fluoride-containing material to the surface of said molten aluminium for entry into said vortex

(3) continuing the stirring of the molten aluminium until the alkali metal and alkaline earth metal content is reduced to a desired low level

(4) separating the molten Al from the molten fluoaluminate reaction products.

2. A method according to claim 1, further characterised in that the vortex is established eccentrically in relation to the geometric axis of the containing vessel.

3. A method according to claim 1 or 2, further characterised in that said vortex is established and maintained by means of a multi-blade impeller having blades which are inclined in relation to the axis of impeller rotation.

4. A method according to any preceding claim, further characterised in that the molten metal is treated with powdered AlF_3 or $\text{NaF} \cdot \text{AlF}_3$ having a low NaF/AlF_3 ratio by weight.

5. A method according to claim 3 further characterised in that the containing vessel is non-cylindrical and has a minimum internal diameter D , and is filled with the molten body of metal to a height H , and the impeller has a diameter d and a blade height h , such that the ratio d/D is between 0.1 and 0.6 and the ratio h/H is between 0.1 and 0.7, D and d being measured in the plane of impeller rotation and H and h being measured along the axis of impeller rotation.

6. A method according to claim 5 further characterised in that the minimum spacing between the axis of impeller rotation and the vessel wall is $D/4$, measured in the plane of impeller rotation.

7. A method according to claim 5 further characterised in that the midpoint of said blades is spaced above the bottom of said vessel by a distance y , measured along the axis of impeller rotation, said distance y being $0.25H$ and $0.75H$.

8. A method according to claim 5 further characterised in that the axis of impeller rotation is eccentric in relation to the vessel axis by a distance, x , having a value of $0.25 - 0.6 d$ in the plane of impeller rotation.

9. Apparatus for mixing particulate aluminium fluoride-yielding material with molten aluminium to remove dissolved contaminant alkali metals and alkaline earth metals from the molten aluminium said apparatus comprising

- (a) a non-cylindrical vessel, having a vertical geometric axis and minimum internal diameter D , for containing a body of molten aluminium to a height H above the floor of the vessel; said vessel being essentially free from internal baffles and having a generally rounded interior surface.

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- (b) a cover for said vessel supporting a multi-bladed impeller and means for driving said impeller about a vertical axis and means for rotating the impeller, said impeller having a diameter, d , and its blades having a height, h , the midpoint of said blades being spaced above the floor of the vessel by a distance, y , the axis of impeller rotation being spaced from said geometric axis by a distance x , and said blades having major surfaces pitched downwardly at an angle θ to the vertical;
- (c) the values of d , D , h , H , x and θ being such that d/D is between 0.1 and 0.6, h/H is between 0.1 and 0.7, x is between 0.1 - 0.25 D , y is between 0.25 H and 0.75 H , and θ is between 0° and 45° in relation to the impeller axis.
- (d) the minimum spacing between the axis of rotation of the impeller and the vessel, measured in the plane of impeller rotation, is $D/4$, the values of D , d and x being measured in the plane of impeller rotation, the values of H and h being measured along the impeller axis of rotation.

10. Apparatus according to claim 9, further characterised in that d/D is between 0.15 and 0.40, h/H is between 0.2 and 0.40, x is 0.25 - 0.7 d , y is between 0.4 H and 0.6 H , and θ is between 30° and 40° .

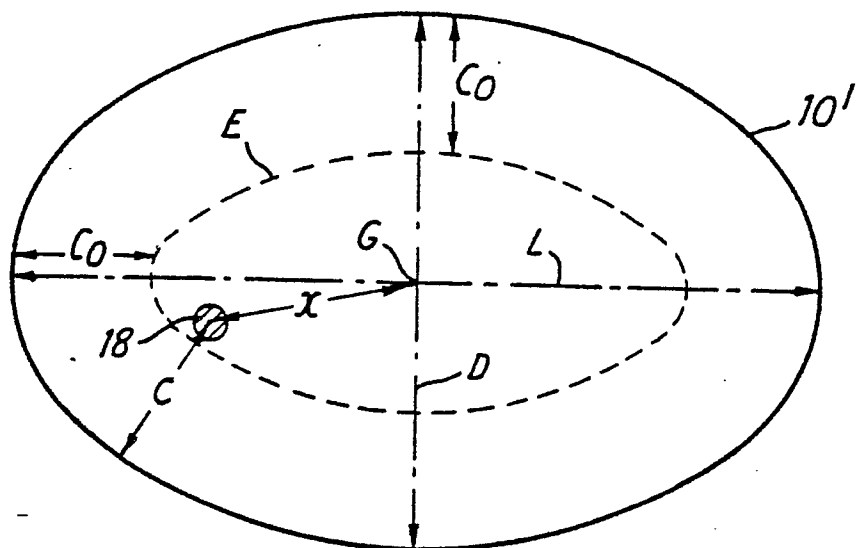


FIG. 1

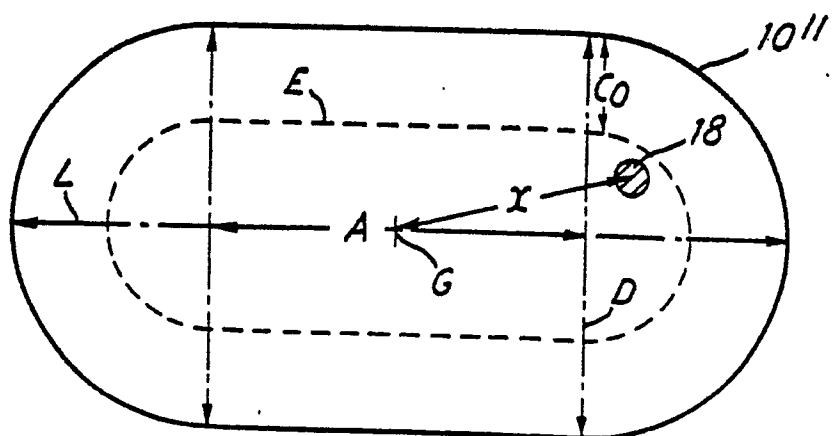
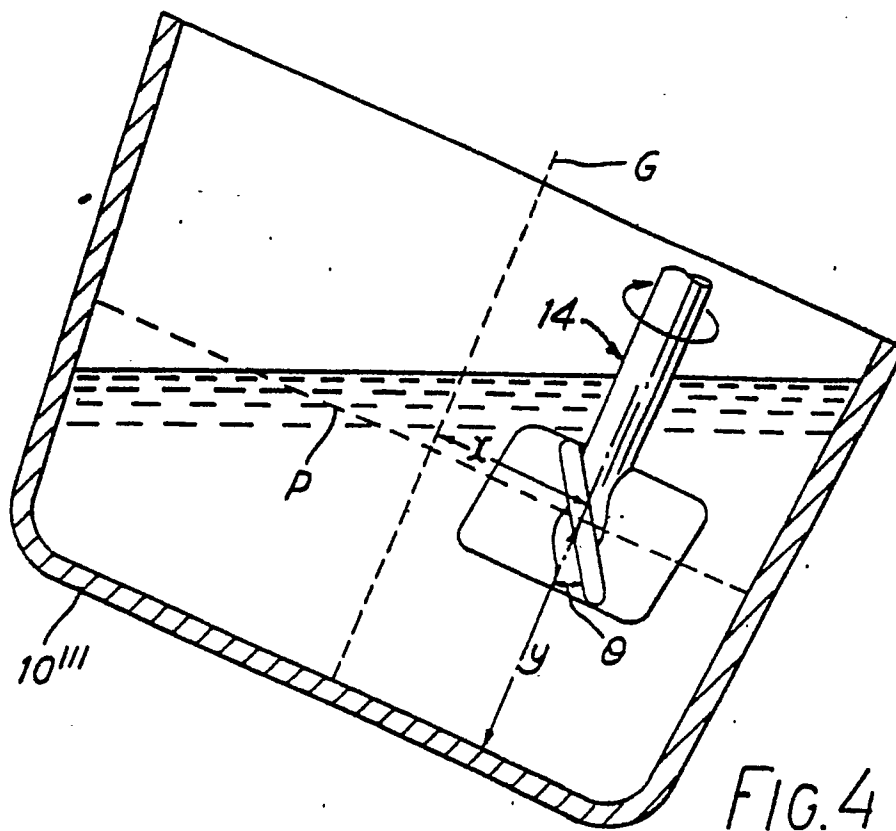
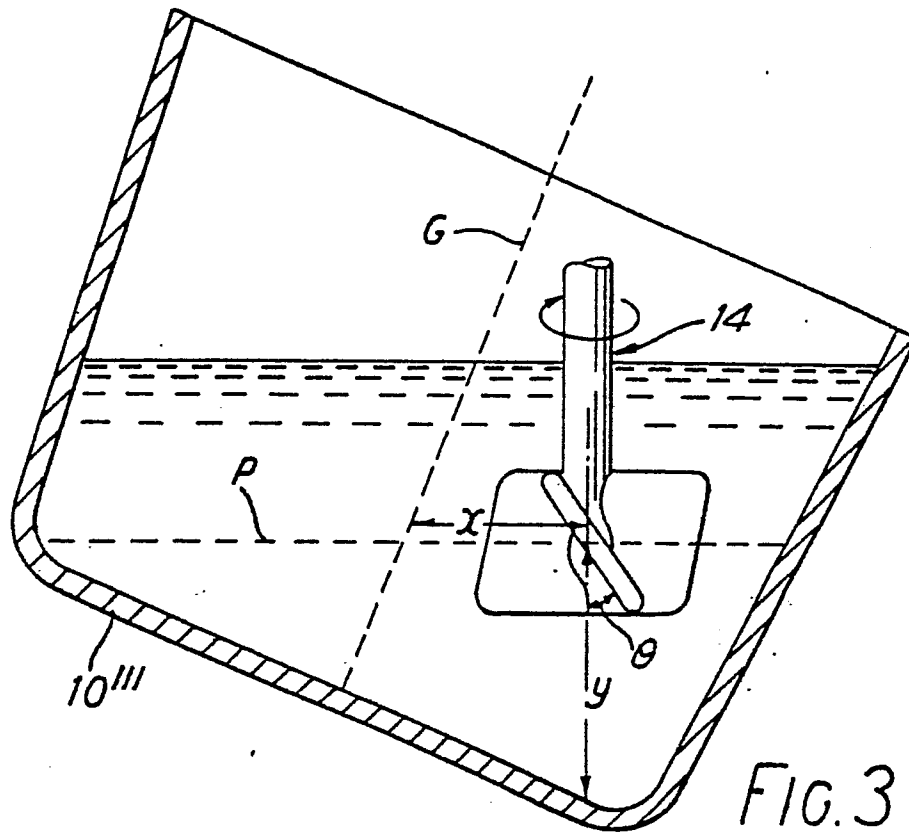


FIG. 2



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EUROPEAN SEARCH REPORT

Application number

EP 82 30 5965

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
D, E	EP-B-0 065 854 (ALCAN) * Whole document *	1-10	C 22 B 21/06 F 27 D 23/04
X, Y	--- US-A-3 459 536 (R.E. TOUZALIN) * Claims; figures 6, 7 *	1, 3, 9	
Y	--- US-A-4 058 394 (P.B. CRIMES) * Claims; figures *	1, 5-7, 9	
Y	--- GB-A-1 367 069 (THE BRITISH ALUMINIUM CY.) * Claims; figures *	4	
A	--- DE-A-2 707 437 (KENNECOTT) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 22 B F 27 D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16-06-1983	Examiner JACOBS J.J.E.G.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			