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(54) Title: PROCESS FOR RECOVERING ALKALINE SOLUTIONS

(57) Abstract: Process for the recovery of spent alkaline baths or solutions, in particular spent solutions of soda (NaOH) or potash (KOH) coming from aluminium pickling reactions, in particular from the treatment of extrusion dies used in the extrusion of aluminium, which comprises a first phase of a) treatment of the spent soda bath or solution with carbon dioxide (CO2), obtaining a first precipitate and a first solution, b) treatment of said first solution with oxides and/or hydroxides of divalent metals, obtaining a second precipitate and a second solution of soda (NaOH) or potash (KOH) which can be re-used without further treatment.

"PROCESS FOR RECOVERING ALKALINE SOLUTIONS"

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SUBJECT OF THE INVENTION

The present invention concerns a process for the treatment and recovery of alkaline solutions, in particular solutions based on caustic soda or caustic potash, used in aluminium pickling reactions.

STATE OF THE ART

Metalworking processes provide a number of obligatory stages necessary to make the metal suitable for the subsequent work processes or the subsequent surface treatments. A very important stage in metal and metal alloy work processes is represented, for example, by chemical pickling which, again by way of example, promotes adhesion and long-term strength of glues and paints.

In particular in the case of aluminium and its alloys, pickling operations are performed in an alkaline environment, mainly by caustic soda or caustic potash solutions. Furthermore, the same alkaline solutions of caustic soda and/or potash are widely used in the case of extrusion of aluminium sections, a particular application of the technique known as extrusion which is one of the fundamental techniques of the entire manufacturing industry. In short, the process of extrusion consists in compressing the metal to be worked by means of a die, producing a deformation thereof which gives it an appearance and profile according to the desired dimensions and forms. Said deformation is imparted from the outside and, if a hollow product is required, also from the inside by the insertion of a core. Said process provides compression of the starting materials, after heating which facilitates the modelling thereof, inside a cylinder or die terminating in a shaped hole which gives the material the desired form. The section thus obtained after extrusion undergoes further finishing and, if necessary, painting, before it is put on the market. The extrusion of aluminium profiles therefore combines one of the basic techniques of industrial processing with one of the materials, aluminium, most universally widespread in the production of articles of all types, from simple saucepans to very complicated components of jet engines. In any case, the extrusion of aluminium

sections constitutes the first step in the production of numerous daily-used articles, including saucepans, as mentioned above, tin cans and door and window frames commonly used in homes.

As described above, the process of extrusion of metals, in particular the process of extrusion of aluminium, involves the use of dies suitable for giving the metal the desired form. Once the programmed extruded parts have been obtained, the residue left inside the channels of the extrusion die must be eliminated before performing the next extrusion operation.

Generally the die is immersed in a bath, also called pickling bath. The operating principle of this bath, in the case of aluminium, is based on the chemical reaction which occurs between metallic aluminium and NaOH (sodium hydroxide or caustic soda) or KOH (potassium hydroxide or caustic potash) in an aqueous solution. In practice, the soda or the potash react with the aluminium and form $NaAlO_2$ or $KAlO_2$ with the formation of gaseous hydrogen. In this way the aluminium accumulated in the die dissolves and the die is cleaned and is ready to be used again. As the soda or potash bath is used, the free soda or potash is consumed and its concentration decreases. When the concentration of free soda or potash reaches the minimum level below which the pickling bath is no longer able to perform its function, the bath is spent and must be replaced, with high costs and considerable disposal problems.

At this point, there is the problem of disposing of or recovering the bath or spent soda or potash solution. The systems of disposal and/or recovery currently most widely used can be schematised as follows.

1) Disposal after purification treatment, which involves high costs and difficulty in disposing of the solution, even after purification.

2) The spent bath is "corrected" and then used as "flocculant" in purification plants. This system has no commercial value, in the sense that the "corrected" bath is given away free of charge, although disposal has to be paid for. In addition to being non-remunerative in financial terms, this method also involves significant disposal problems.

3) Recovery of the spent bath by means of two different systems:

3.1) dilution

3.2) transformation

In the first case (3.1), the spent soda solution is diluted with water, in a ratio of approximately 1:100. This causes the precipitation of $Al(OH)_3$ which is partially filtered and removed while the remaining solution can be re-used, even though it contains dissolved quantities of $Al(OH)_3$ which can interfere, especially if re-use is repeated. In this case, however, the soda or potash solution obtained from the above-mentioned recovery process is very diluted and cannot be used as it is but must be concentrated by means of evaporation, with considerable costs due to the required energy consumption. Alternatively, the diluted solution can be concentrated by means of a process of reverse osmosis, but also in this case the costs are high and the results uncertain due to the presence of traces of aluminium which are dangerous as they can cause collapse of the osmotic membranes.

Alternatively to dilution, the spent soda or potash solution can be chemically transformed (3.2) via the addition of carbon dioxide (CO_2). In this case, the chemical reactions involved provide transformation of the residual soda (NaOH) or potash (KOH) into sodium carbonate (Na_2CO_3) or potassium carbonate (K_2CO_3) with formation of water, and likewise the transformation of $NaAlO_2$ or $KAlO_2$ (which forms by reaction between soda or potash and aluminium) into sodium carbonate (Na_2CO_3) or potassium carbonate (K_2CO_3) and aluminium hydroxide ($Al(OH)_3$) which precipitates and can be filtered and removed. In this way a final solution is obtained rich in sodium carbonate or potassium carbonate which can be integrated with soda or potash and re-used in the treatment of pickling dies. The limit of this method is represented by the fact that, over time, sodium carbonate or potassium carbonate accumulates in the solution, until further use becomes impossible. At this point, the problem of disposal arises again and a new soda or potash solution has to be used, with high costs and considerable inconvenience. This transformation process allows the same solution, appropriately treated, to be re-used for a limited number of times but poses the problem of disposal and involves the need to provide new solutions for treatment of the dies.

OBJECTS OF THE INVENTION

The object of the present invention is to provide a process for the recovery of spent alkaline baths or solutions coming from aluminium pickling reactions, in particular from the treatment of extrusion dies used in the extrusion of aluminium, which allows recovery of the solutions with consequent re-use of the same.

A further object of the present invention is to provide a process for the recovery of spent alkaline baths or solutions coming from aluminium pickling reactions, in particular from the treatment of extrusion dies used in the extrusion of aluminium, which does not provide the substantial correction, integration or concentration of the solution recovered.

A further object of the invention is to provide a process for the recovery of spent alkaline baths or solutions coming from aluminium pickling reactions, in particular from the treatment of extrusion dies used in the extrusion of aluminium, which is economically advantageous and which involves a significant economic advantage throughout the extrusion process.

A further object of the present invention is to provide a process for the recovery of spent alkaline baths or solutions coming from aluminium pickling reactions, in particular from the treatment of extrusion dies used in the extrusion of aluminium, which is simple, does not require the use of particular reagents and can be performed parallel to any extrusion process.

A further object of the present invention is use of the above-mentioned process, for recovery of the spent alkaline baths or solutions coming from aluminium pickling reactions, in particular from the treatment of extrusion dies used in the extrusion of aluminium.

DISCLOSURE

These and further objects and relative advantages which will be better highlighted in the following description are obtained by a process for the recovery of spent alkaline baths or solutions, in particular spent solutions of caustic soda (NaOH) or caustic potash (KOH) coming from operations of alkaline pickling/degreasing of articles made of aluminium and/or its alloys. Said operations are performed, for example, in the following sectors:

1) removal of aluminium and its alloys from extrusion dies
2) alkaline degreasing/pickling prior to anodic oxidation of aluminium and its alloys
3) lightening and alkaline chemical milling of aluminium and its alloys in general and in the aeronautical and military sectors in particular
4) alkaline degreasing/pickling of aluminium strip or sheet prior to painting or anodic oxidation, or as a stand-alone process.

The process comprises a first phase of:

a) treatment of the spent bath or soda or potash solution with carbon dioxide (CO2), obtaining a first precipitate and a first solution,

b) treatment of said first solution with oxides and/or hydroxides of divalent metals, obtaining a second precipitate and a second solution.

According to the present invention, said second solution thus obtained is directly used in the processes in the previous points 1,2,3,4, without the need to be concentrated, corrected or in any way modified.

More specifically, said phase a), when conducted on spent soda or potash solutions coming from the above-mentioned treatments, provides the following chemical reactions:

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O \text{ or}$$

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

$$2NaAlO_2 + CO_2 + H_2O \longrightarrow Na_2CO_3 + 2Al(OH)_3 \text{ or}$$

$$2KAlO_2 + CO_2 + H_2O \longrightarrow K_2CO_3 + 2Al(OH)_3$$

where said first precipitate is represented by $2Al(OH)_3$, while said first solution comprises Na_2CO_3 or K_2CO_3. Said first precipitate is advantageously eliminated by filtration, while the resulting solution, rich in sodium or potassium carbonate, directly undergoes said phase b). In particular, according to the invention, when said oxides and/or hydroxides of divalent metals are chosen like CaO and/or $Ca(OH)_2$, said

phase b) provides the following chemical reactions:

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2NaOH \text{ or}$$

$$K_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2KOH$$

$$Na_2CO_3 + CaO + H_2O \longrightarrow CaCO_3 + 2NaOH \text{ or}$$

$$K_2CO_3 + CaO + H_2O \longrightarrow CaCO_3 + 2KOH$$

The calcium carbonate ($CaCO_3$) is obtained in the form of a precipitate (called second precipitate), which is removed by filtration, while the resulting solution (called second solution), is re-used as it is being rich in soda or potash.

According to the present invention, it is therefore possible to carry out a process for the recovery of spent alkaline solutions, in particular soda or potash, used for aluminium pickling reactions, in particular in the treatment and cleaning of extrusion dies used in the extrusion of aluminium, in addition to the other operations in accordance with points 2,3,4.

This process has considerable advantages with respect to the processes in the known art.

In fact, it is possible to fully re-use the initial soda or potash solution without the need to perform additional operations and treatments, with consequent saving in time and also considerable economic savings.

A further advantage is represented by the fact that it is not necessary to provide for disposal of the spent solution, with consequent cost savings and advantages also in terms of general management of the industrial process.

A further advantage is represented by the fact that, operating according to the process subject of the present invention, all the $Al(OH)_3$ forming during phase a) of said process is removed by filtration or in any case by separation, since it is a precipitate (first precipitate). As the solution does not undergo dilutions, there is no risk of a part of said Al hydroxide re-dissolving or remaining directly in solution and therefore remaining, even only partially, present in said first solution.

The spent starting solution can advantageously be optionally diluted with water up to

a ratio of 1:1. This dilution can be advantageous because it is an aid for avoiding the precipitation of Na_2CO_3 or KCO_3 in crystallised form during the reaction in the above-mentioned stage a). If said dilution is performed, the solution resulting from stage b), and therefore the final solution, will undergo an optional concentration phase c) which will occur, for example, by evaporation, until reaching the desired soda or potash concentration for re-use of the solution.

Said optional evaporation stage, and relative preceding optional dilution stage, does not involve the drawbacks due to the dilution when performed according to the methods described above and commonly employed in the known art.

In fact, while in the processes of dilution according to the known art a dilution is performed in a ratio of approximately 1:100, according to the present invention the dilution ratio does not exceed 1:1 and, consequently, also any possible phase of concentration of the final solution is very simple, rapid and with practically non-existent added costs.

A further advantage is represented by the fact that, even if said optional stage of dilution of the starting solution and said optional phase of concentration of the final solution (or said second solution) is performed, any dilution is in a ratio of 1:1 and all the aluminium hydroxide ($Al(OH)_3$) will remain in the form of a precipitate and can therefore be completely removed. In other words, even if dilution is performed as indicated above, there will be no problem with part of the Al hydroxide dissolving, as occurs using the known techniques. In fact, the dilution is such as to guarantee that all the $Al(OH)_3$ formed is removed in the form of a solid precipitate.

The above will be more clearly described with the help of the following examples of practical embodiment, provided only by way of non-limiting example of the present invention.

EXAMPLE 1

Process for recovery of a spent NaOH bath

Starting solution

Spent aluminium extrusion die pickling bath.

Contents of the solution

Free NaOH	15-30%
Al (in the form of $NaAlO_2$)	3-15%

Carbonaceous and oily extrusion residues

- The process allows separation of aluminium in the form of pure hydroxide and re-use thereof as a second raw material. It also allows complete recovery of the free and combined NaOH.
- The process provides an optional pre-filtration phase, followed by a phase of neutralisation of the spent solution according to the following reaction schemes:

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

$$2NaAlO_2 + CO_2 + H_2O \longrightarrow Na_2CO_3 + 2Al(OH)$$

- Where for each 1Kg of NaOH it is necessary to add 0.55 Kg of CO_2 and for each 1Kg of Al it is necessary to add 0.81 Kg of CO_2.
- The phase of filtering of $Al(OH)_3$ (which precipitates completely) can advantageously be performed by means of a belt, rotating drum, centrifuge or bag filter. The pure hydroxide which is thus obtained is advantageously used as a second raw material since it is free of other contaminants.
- The soda regeneration phase is performed by reaction of the solution containing Na_2CO_3 with CaO or with $Ca(OH)_2$, according to the following reactions:

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2NaOH$$

$$Na_2CO_3 + CaO + H_2O \longrightarrow CaCO_3 + 2NaOH$$

- For example, the starting concentration in Na_2CO_3 is between 5 and 25%, while the quantity of CaO used for each Kg of Na_2CO_3 is 0.528 Kg. The reaction temperature is between 40 and 100°C and the reaction time can vary between 10 minutes and 3 hours. The solution of caustic soda thus regenerated will have a concentration of between approximately 2.5% and 15%. If necessary, the final solution can be concentrated to the desired value (between 5 and 30%), for example by means of steam or hot water concentrator in heat pump or multi-stage evaporators.
- The soda solution thus recovered can be for example stored in a metal, PVC, PP, fibreglass or SS silo. The titre of the solution can be controlled for example by means of acidimetric titration. The controls highlight the following residues: Al 10-1000 ppm, Ca 10-300 ppm.

EXAMPLE 2

Process for recovery of a spent KOH bath

Starting solution

Spent aluminium extrusion die pickling bath.

Contents of the solution

Free KOH	15-30%
Al (in the form of $KAlO_2$)	3-15%

Carbonaceous and oily extrusion residues

- The process allows separation of aluminium in the form of pure hydroxide and re-use thereof as a second raw material. It also allows complete recovery of the free and combined KOH.
- The process provides an optional pre-filtration phase, followed by a phase of neutralisation of the spent solution according to the following reaction schemes:

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

$$2KAlO_2 + CO_2 + H_2O \longrightarrow Na_2CO_3 + 2Al(OH)_3$$

- Where for each 1Kg of KOH it is necessary to add 0.39 Kg of CO_2 and for each 1Kg of Al it is necessary to add 0.81 Kg of CO_2.
- The phase of filtering of $Al(OH)_3$ (which precipitates completely) can advantageously be performed by means of a belt, rotating drum, press, centrifuge or bag filter. The pure hydroxide which is thus obtained is advantageously used as a second raw material since it is free of other contaminants.
- The potash regeneration phase is performed by reaction of the solution containing K_2CO_3 with CaO or with $Ca(OH)_2$, according to the following reactions:

$$K_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2KOH$$

$$K_2CO_3 + CaO + H_2O \longrightarrow CaCO_3 + 2KOH$$

- For example, the starting concentration in K_2CO_3 is between 5 and 25%, while the quantity of CaO used for each Kg of K_2CO_3 is 0.40 Kg. The reaction temperature is between 40 and 100°C and the reaction time can vary between 10 minutes and 3 hours. The solution of caustic potash thus regenerated will have a concentration of between approximately 2.5% and 15%.
- If necessary, the final solution can be concentrated to the desired value (between 5 and 30%), for example by means of steam or hot water concentrator in heat pump or multi-stage evaporators.
- The potash solution thus recovered can be stored, for example, in a metal, PVC, PP, fibreglass or SS silo. The titre of the solution can be controlled for example by means of acidimetric titration. The controls highlight the following residues: Al 10-1000 ppm, Ca 10-300 ppm.

EXAMPLE 3

Process for recovery of a spent NaOH bath – Specific Case

ANALYSIS OF THE SPENT SOLUTION

- free NaOH 15.5 %
- $NaAlO_2$ 15.18% (Al= 5%)
- d = 1.28

Note: The content of free + combined NaOH is therefore equal to 23%.

PROCESS SEQUENCE:

1) PREPARATION OF SOLUTION "A"
2) CARBONATION REACTION AND PRECIPITATION OF $Al(OH)_3$
3) FILTRATION OF THE PRECIPITATE (SLUDGE)
4) NaOH REGENERATION REACTION
5) RECONCENTRATION OF NaOH SOLUTION

1) *PREPARATION OF SOLUTION "A"*

- 1 Kg spent solution
- 1 Kg mains H_2O

2) *CARBONATION REACTION AND PRECIPITATION OF $Al(OH)_3$*

Insufflation of CO_2 according to the following reactions:

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

$$2NaAlO_2 + CO_2 + 3H_2O \rightarrow Na_2CO_3 + 2Al(OH)_3 \downarrow \text{ (precipitate)}$$

- The reaction required, in accordance with the stoichiometry, a total of 126.5 grams of CO_2
- Reaction temperature 20°C
- CO_2 pressure: 1.5 bars

3) *FILTRATION OF THE PRECIPITATE (SLUDGE)*

- After filtration the following were measured:
  Quantity of sludge $Al(OH)_3$ (d.r.=100%) obtained : 144.4 g
  Quality of sludge obtained : $Al(OH)_3$ 8.5%

- The filtered solution was then analysed and found to contain exclusively:
  Na_2CO_3 286.47g (13.56% against a theoretical 15.2%): yield 94%
  Al (<10 ppm)
  H_2O balance to 2000g

4) NaOH REGENERATION REACTION

¤ Predicted reaction

$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3 \downarrow$ (precipitated as sludge)

¤ Reaction conditions

- Quantity of hydrated lime required: 212.8 g
- Reaction temperature : 80° ~ 90° C
- Reaction time : 60'

¤ Results of the reaction:

- Quantity of sludge ($CaCO_3$) obtained: 287.5 g (D.R. 100%)
- Quality of sludge : ($CaCO_3$ 99.3%)
- The solution brought to volume with distilled H_2O, filtered, was analysed and found to contain:

NaOH 204.7 g (concentration 10.325%, against a theoretical 10.81%) yield 95%

Al below 0.5%

H_2O balance to 2000 g

5) RECONCENTRATION OF NaOH SOLUTION

¤ Reaction conditions:

- Concentration by evaporation

- Temperature 100°C
- % of evaporate 50%

¤ Reaction result

- NaOH 201.5 g (20.15% against a theoretical 20.4%) yield 97.7%
- Al below 1%
- Ca below 1%
- Na_2CO_3 residual: 1.9 %
- H_2O balance to 1000 g

A) PRACTICAL RESULTS OF THE PROCESS:

¤ Quantity of reagents used:

- CO2 126.5 g
- Ca(OH)2 212.8 g

¤ Quantity of sludge obtained

- From reaction 2 (Al (OH)3) : 144.4 g
- From reaction 4 (CaCO3) : 287.5 g

¤ Quantity of NaOH regenerated:

- 20.4% (with a yield of 88.6%)

¤ Quality of NaOH regenerated

- Al, Calcium below 1%
- Residual Na_2CO_3 1.9%

¤ Final yield

- Total initial NaOH : 23 %
- NaOH after regeneration : 20.15%
- Final yield : 88%

EXAMPLE 4

Process for recovery of a spent KOH bath – Specific Case

ANALYSIS OF THE SPENT SOLUTION

- Free KOH 15.5%
- $KAlO_2$ 18.5% (Al= 5%)
- d = 1.28

Note: The content in free + combined KOH is therefore equal to 32.2%.

PROCESS SEQUENCE:

1) PREPARATION OF SOLUTION "A"
2) CARBONATION REACTION AND PRECIPITATION $Al(OH)_3$
3) FILTRATION OF THE PRECIPITATE (SLUDGE)
4) KOH REGENERATION REACTION
5) RECONCENTRATION OF KOH SOLUTION

1) *PREPARATION OF SOLUTION "A"*

- 1 Kg spent solution
- 1 Kg mains H_2O

2) *CARBONATION REACTION AND PRECIPITATION $Al(OH)_3$*

Insufflation of CO_2 according to the following reactions

$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$$

$2KAlO_2 + CO_2 + 3H_2O \rightarrow K_2CO_3 + 2Al(OH)_3 \downarrow$ (precipitate)

- The reaction required, in accordance with the stoichiometry, a total of 84 grams of CO_2
- Reaction temperature 20°C
- CO_2 pressure: 1.5 bars

3) FILTRATION OF THE PRECIPITATE (SLUDGE)

- After filtration, the following were measured:

Quantity of sludge $Al(OH)_3$ (d.r.=100%) obtained : 144.4 g
Quality of the sludge obtained : $Al(OH)_3$ 8.5%

- The filtered solution was then analysed and found to contain exclusively:

K_2CO_3	358 g (17.9% against a theoretical 19.04%: yield 94%)
Al	(<10 ppm)
H_2O	balance to 2000 g

4) KOH REGENERATION REACTION

¤ Predicted reaction

$K_2CO_3 + Ca(OH)_2 \rightarrow 2KOH + CaCO_3 \downarrow$ (precipitated as sludge)

¤ Reaction conditions

- Quantity of hydrated lime required : 200 g
- Reaction temperature : 80° ~ 90° C
- Reaction time : 60'

¤ Results of the reaction:

▪ Quantity of sludge ($CaCO_3$) obtained: 270 g (D.R. 100%)

▪ Quality of sludge : ($CaCO_3$ 99.3%)

▪ The solution brought to volume with distilled H_2O, filtered, was analysed and found to contain:

•KOH 305.9 g (concentration 15.2%, against a theoretical 16.1%) yield 95%

•Al below 0.5%

•H_2O balance to 2000 g

5) <u>RECONCENTRATION OF KOH SOLUTION</u>

¤ Reaction conditions:

- Concentration by evaporation
- Temperature 100°C
- % of evaporate 50%

¤ Reaction result

- KOH 299 g (29.9% against a theoretical 30.59%: yield 97.7%)
- Al below 1%
- Ca below 1%
- K_2CO_3 residual: 1.9 %
- H_2O balance to 1000 g

A) PRACTICAL RESULTS OF THE PROCESS:

¤ Quantity of reagents used:

- CO_2 84 g
- $Ca(OH)_2$ 200 g

¤ Quantity of sludge obtained

- From reaction 2 : Al(OH)3 : 144.4 g
- From reaction 4 : CaCO3 : 270 g

¤ Quantity of KOH regenerated:

- 29.9% (with yield equal to 92.8%)

¤ Quality of KOH regenerated:

- Al, Calcium below 1%
- K_2CO_3 residual 1.9%

¤ Final yield

- Total initial KOH : 32.2%
- KOH after regeneration : 29.9%
- Final yield : 92.8%

CLAIMS

1. A process for the recovery of spent alkaline baths or solutions, coming from aluminium pickling reactions, which comprises a first step of:

a) treating said spent alkaline bath or solution with carbon dioxide (CO2), obtaining a first precipitate and a first solution,

and a second step of:

b) treating said first solution with oxides and/or hydroxides of divalent metals, obtaining a second precipitate and a second solution.

2. The process according to claim 1, characterized in that said pickling reactions comprise reactions for treating extrusion dies used in the extrusion of aluminium.

3. The process according to claim 1, characterized in that said spent alkaline baths or solutions are spent baths or solutions of caustic soda (NaOH) or caustic potash (KOH).

4. The process according to claim 1, characterized in that said metal is aluminium.

5. The process according to claims 3 and 4, characterized in that said first precipitate is aluminium hydroxide (Al(OH)3) and said first solution is a solution of sodium carbonate (Na_2CO_3) or potassium carbonate (K_2CO_3).

6. The process according to claim 5, characterized in that said oxides and/or hydroxides of divalent metals are CaO and/or $Ca(OH)_2$.

7. The process according to claim 6, characterized in that said second precipitate is calcium carbonate $CaCO_3$ and said second solution is a solution of soda (NaOH) or potash (KOH).

8. The process according to the preceding claims, characterized in that said first and second steps take place according to the following chemical reactions:

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O \text{ or}$$

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

$$2NaAlO_2 + CO_2 + H_2O \longrightarrow Na_2CO_3 + 2Al(OH)_3 \text{ or}$$

$$2KAlO_2 + CO_2 + H_2O \longrightarrow K_2CO_3 + 2Al(OH)_3$$

$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2NaOH$ or

$K_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2KOH$

$Na_2CO_3 + CaO + H_2O \longrightarrow CaCO_3 + 2NaOH$ or

$K_2CO_3 + CaO + H_2O \longrightarrow CaCO_3 + 2KOH$

9. The process according to the preceding claims, characterized in that said first and said second precipitate are removed by filtration.

10. The process according to the preceding claims, characterized in that it comprises an initial dilution step and an optional concentration step c) of said second solution.

11. The process according to claim 10, characterized in that said dilution step takes place with water with a ratio from 1:0.5 to 1:10.

12. The process according to the preceding claims, characterized in that said spent alkaline bath or solution is a solution of soda NaOH or potash KOH in concentrations of free soda or potash comprised between 15 and 30%, the concentration of said first solution of sodium carbonate Na_2CO_3 or potassium carbonate K_2CO_3 is comprised between 0.7 and 40%, the reaction temperature in said second step b) is between 40 and 100°C and the reaction time is between 10 minutes and three hours, obtaining said second solution of soda NaOH or potash KOH at a concentration comprised between 0.7 and 30%.

13. Use of said second solution according to the preceding claims for aluminium pickling reactions.

14. Use of said second solution according to the preceding claims for treating extrusion dies used in the extrusion of aluminium.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2010/001015

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23F1/46 C23G1/36 C01D1/22 C01D1/32 C01F7/14
B21C35/06
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)
C23F C23G C01D C01F B21C

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 practical, search terms used)
EPO-Internal, WPI Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	CN 1 287 186 A (TAN HONGWEI [CN]) 14 March 2001 (2001-03-14) the whole document	1,3-13 2
X Y	DE 197 03 348 A1 (KLEIN KLAUS DIPL ING [DE]) 6 August 1998 (1998-08-06) column 1, line 30 - column 2, line 56; claims	13,14 1-12
Y	DE 27 38 134 B1 (VAW VER ALUMINIUM WERKE AG) 8 February 1979 (1979-02-08) the whole document	1-12
A	EP 1 932 948 A1 (ITALTECNO S R L [IT]) 18 June 2008 (2008-06-18) paragraph [0001] - paragraph [0003] paragraph [0017] - paragraph [0060]; claims	1-14

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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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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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
29 July 2010	05/08/2010

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2010/001015

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 607 482 A (SELM ROBERT P) 21 September 1971 (1971-09-21) the whole document	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2010/001015

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