(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 032 886**
A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **81850009.2**

(51) Int. Cl.³: **C 23 G 1/36**

(22) Date of filing: **16.01.81**

(30) Priority: **18.01.80 SE 8000444**

(43) Date of publication of application: **29.07.81**
Bulletin 81/30

(84) Designated Contracting States: **AT BE CH DE FR GB IT LI LU NL SE**

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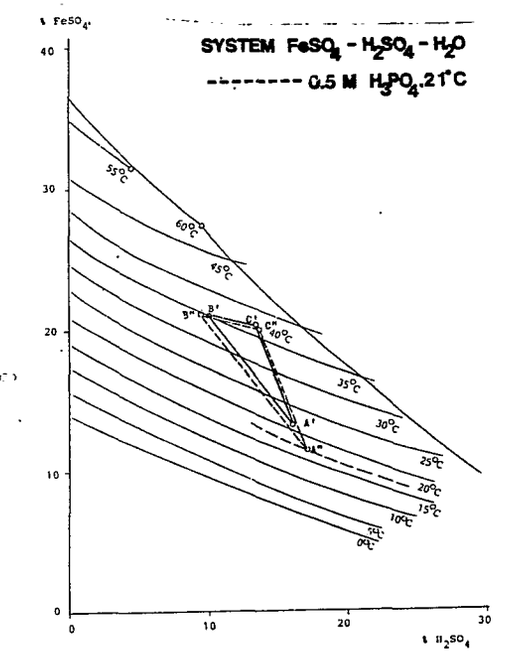
(54) A method of regenerating pickling solutions.

(57) The invention relates to a method for regenerating by crystallization on cooling pickling bath solutions based on sulphuric acid or hydrochloric acid and used for pickling iron, steel and other iron alloys. According to the invention the bath solution is regenerated in a combination of three stages. In a first stage acid is added to the solution in a concentration higher than the acid concentration of said solution, and the content of phosphoric acid is adjusted to be maintained between about 0.01 and 1 mole per litre solution, thereby to approach or to exceed the solubility of difficultly dissolved iron salts corresponding to the acid. In a second stage the solution is cooled, whereby iron salts precipitate. The cooling process is effected so as to reach a temperature at which the contents of iron and acid in the residual solution are suitable to permit said solution to be used again for pickling purposes. In a third stage the precipitated iron salt is removed from the solution, whereafter the regenerated pickling solution is returned for use at the pickling process.



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A METHOD OF REGENERATING PICKLING SOLUTIONS.

The present invention relates to a method of regenerating by crystallization on cooling pickling bath solutions based on sulphuric acid and/or hydrochloric acid and used for pickling iron, steel and other iron alloys.

Acid pickling processes are applied within the iron and steel industries and the workshop industry for surface treating articles made of iron, steel and other iron alloys. In the steel industry, acid pickling processes are primarily applied in order to dissolve the scale and other oxide and hydroxide layers formed on the metal surfaces of workpieces during the various processes of their manufacture. These layers are mainly the result of the thermal treatment processes to which the workpieces are subjected, e.g. to annealing processes and subsequent rolling operations.

In the workshop industry, workpieces are pickled in acid baths in order to remove rust and other contaminants from the surfaces of the workpieces. The rust is formed during the transportation, storage and handling of the workshop raw materials, these raw materials comprising, for example, finished goods from the steel industry or intermediate products from other metal-processing industries, e.g. products obtained from different subcontractors. The contaminants originate from the same sources, and may comprise welding, soldering or brazing residues and handprints. They may also originate from oil coatings and other coatings resulting from processing operations and from surface treatment processes carried out in order to afford the steel surfaces of the workpieces some protection against corrosion.

In the steel industry, sulphuric acid and hydrochloric acid pickling solutions are primarily used to pickle non-alloyed steel or low-alloyed steel (commercial steel). Those pickling baths used in the workshop industry are mainly sulphuric-acid solutions.

When scale-coated articles made of non-alloyed or low-alloyed steels are pickled in acid pickling baths, the scale is first partially dissolved at the same time as the major part of said scale is removed mechanically by the development of hydrogen gas in pores and cavities in the scale. The thus exposed surfaces of the basic material are then liable to attack by the acid, and if the pickling process is not stopped at the correct point of time an unnecessarily large quantity of material is consumed, without any advantage being gained thereby.

In normal cases the concentration of the solution and the temperature at which the pickling process is carried out are those given in the following table:

Pickling acid	Concentration mol/l	Temperature °C
Hydrochloric acid	2-5	20-60
Sulphuric acid	1-2.5	60-90

The pickling time for the complete removal of scale in a rolling mill is about 1 minute.

When pickling workpieces to remove rust therefrom, rust and other contaminants on the surfaces of the workpiece are progressively dissolved, and the conditions are somewhat different to those when pickling in order to remove scale. Normal concentrations and temperatures are given in the following table:

Pickling acid	Concentration mol/l	Temperature °C
Hydrochloric acid	1-4	20-60
Sulphuric acid	0.5-1	20-80

The time required when pickling to remove rust is normally between 5 and 20 minutes.

One common feature of all pickling processes is that when the raw metal surface is exposed it is readily attacked by the acid, resulting in an unnecessary loss of material by dissolution of the metal. To avoid this it is normal to add an organic inhibitor, sometimes referred to as a restrainer, whose purpose is to block the exposed, free metal surface by adsorption thereon, thereby to protect said surface from acid attack.

Described in European Patent Application No. 80850166.2 is a method for acid-pickling metallic material having > 80 % Fe while simultaneously inhibiting the exposed metal surfaces against dissolution by acid attack. According to this method the material are brought into contact with an aqueous solution containing phosphoric acid and one or both of the mineral acids hydrochloric acid and sulphuric acid. The phosphoric acid concentration is adjusted to at least about 0.01 M (i.e. mol/l) and at most about 1 M, while the total acid concentration is adjusted to the range between about 0.5 and 4 mole per litre.

Irrespective of the pickling acid used, the concentration of acid will decrease as the process proceeds, while the concentration of dissolved iron (and possibly other alloying metals) will increase at the same time. Ultimately the pickling effect will be non-existent or will have decreased to such an extent as to render it no longer possible to utilize the solution for pickling purposes.

Various methods of disposing of the consumed pickling solution are known to the art. These methods are applied technically with differing degrees of success. The methods are either concerned with the destruction of the solution or its regeneration for re-use.

In those methods pertaining to the destruction of the solution, said solution is neutralized by adding lime, sodium hydroxide or some other alkali thereto. At the same time herewith, iron and other metals are precipitated in hydroxide form. Subsequent to separating

the precipitate, the water phase can be discharged to a recipient, while observing those requirements appertaining to the care and protection of the environment. Because of the low economic value of the precipitate, its metal content cannot be utilized. It must therefore be dumped. The disadvantages with the destruction of pickling bath solutions are many, and in a majority of cases obvious, although the costs of the lime and the low economic value of the precipitate are among the most serious of these disadvantages. Hydroxide precipitates are also difficult to handle and are thus particularly difficult to separate from the water phase. Since the acid is neutralized, it cannot be re-used or worked up. Thus, the regeneration of pickling bath solutions is of much more interest in the present context. The different regenerating methods which have been developed thus pertain to the re-use of either residual acid or dissolved metals or, optionally, a combination thereof. The iron content of sulphuric - acid pickling bath solutions can be recovered therefrom in the form of iron sulphates by crystallization. This method, which is the one most used today for working-up pickling bath solutions, requires the crystallization process to be effected either by strong cooling of the solution or by evaporating the solution under a vacuum. Equipment for such methods is commercially available. In one of the previously known methods according to Keramchemie, the crystallization process is carried out in a vacuum crystallizer at a temperature of about $10^{o}C$. In another known crystallization method (The Otto-method) the crystallization of iron sulphate is effected by strong indirect cooling without vacuum in one or more interconnected crystallizers. In both of these methods iron sulphate -heptahydrate is separated from the water phase by centrifugation. The mother liquor is returned to the pickling bath, to which concentrated sulphuric acid is added so as to again obtain suitable pickling conditions.

It is also since long known to regenerate sulphuric acid pickling solutions by first increasing the sulphuric acid content of the pickling solution by supplying concentrated sulphuric acid prior

to a final cooling of the solution in order to crystallize iron sulphate therefrom. Such processes, which for example are disclosed in DE-C-561514 (Sierp and Fränsemeier), DE-B-1124781 (Niedner) and US-A-1589610 (Marsh et al), show much better regenerating efficiency than those using solely the cooling.

However, a common feature of the known crystallization methods is that large quantities of energy are required, since both evaporation and the strong cooling of the bath are unit processes requiring large quantities of heat.

The iron content of hydrochloric-acid pickling bath solutions can be recovered therefrom in the form of iron chlorides or iron oxide.

In the so-called Ruthner-process, described in A Hake, Österr. Chemiker Zeitung 68, 180/85 (1967), for example, a roasting process is applied, in which the spent pickling bath solution is sprayed into a heated reactor space. The water in the solution evaporates and hydrogen chlorine and iron oxide are formed from the metal chlorides and water vapour present, said hydrogen chlorine and iron oxide being removed from the reaction gases by cyclone separation. The hydrogen chlorine gas is absorbed in the water in a column and the obtained hydrochloric acid can be re-used for pickling purposes.

A similar method is described in DE-A-1546164 and 1621615 (Metallgesellschaft AG, Frankfurt), in which the pickling bath solution, subsequent to a certain degree of pre-vaporization, is charged to an oil-heated or gas-heated fluidized bed furnace and there split up while recovering metal oxide and hydrogen chloride from the fumes, by oxidation with an oxygen - containing fluidizing gas.

According to the Pori-process, described in detail in Burtch I W, Iron and Steel Engineer, 50 (1973):4, 40-42 ferrous chloride in the pickling bath solution is oxidized to ferric chloride, which is then hydrolyzed at high temperatures to iron oxide and hydrochloric acid.

Another known method described in NO-A-7302621 concerns the production of iron sulphate from the spent pickling bath by adding sulphuric acid to the bath and electrode-heating said bath to a temperature of 120°C.

It will be evident from the aforedescribed descriptions of the known processes for regenerating pickling bath solutions based on sulphuric acid and hydrochloric acid that present day techniques require very high energy inputs.

Thus, when crystallizing iron sulphate for the treatment of sulphuric acid baths in which the iron is a high concentration and the acid in low concentration, it is necessary to subject the solution to a vacuum or to strong cooling (from about 60°C to about 10°C) or a combination thereof. This requires complicated apparatus, and the installation and operational costs are so high as to render the method unacceptable, at least in the case of pickling installations of average size within the workshop industry. In practice, it is only possible to recover sulphuric acid in those cases when the consumed pickling bath solution is subjected to evaporation processes. In other cases the acid concentration of the residual solution is too low.

The previously described methods available for recovering hydrochloric acid from consumed hydrochloric acid bath solutions require even more energy, even though it is possible by these methods to recover hydrochloric acid with a relatively high degree of efficiency. The practical operation of the kind of apparatus required herefore, is however, extremely complicated.

The object of the present invention is to eliminate the aforementioned disadvantages encountered when regenerating pickling bath solutions based on sulphuric acid and hydrochloric acid, and to provide a technically simple, energy-saving solution to the problems encountered when working-up the pickling bath solution for re-use by the normal user, for example within the workshop industry. Thus, a

further object of the present invention is to utilize the solubility of the iron salts at differing acid concentrations and temperatures and in the presence of phosphoric acid in a manner such as to eliminate such energy-consuming operations as high-temperature splitting, or cooling to low temperatures, when regenerating spent pickling bath solutions. Another object of the invention is to eliminate or reduce the necessity of destroying spent or consumed pickling bath solutions, by using regenerating agents of suitable composition, which, in comparison with previously known methods, provides a method which has a less negative effect on the environment and which requires less energy.

Still another object of the invention is to eliminate the need of complicated and expensive apparatus and to reduce the operational costs of regenerating pickling bath solutions.

It is also an object of the present invention to permit operation of a continuous pickling operation, in which substantially constant pickling conditions can be maintained. According to another object of the invention it is also possible to utilize the iron salts which are precipitated from the pickling solutions, for example as water purifying agents.

It has now surprisingly been found that these objects easily can be realized in a method where the solubility properties of the iron salts in question are utilized in a suitably manner. The method is characterized in that sulphuric acid or hydrochloric acid is added to the solution in a concentration higher than that of said solution in a quantity sufficient to substantially decrease the solubility of the iron salt corresponding to said acid at the temperature in question, in that a content of about 0.01 - 1 mole per litre of phosphoric acid is maintained in the solution, in that the solution is then cooled to a given temperature to crystallize out the iron salt, said temperature being so selected that the solubility of said iron salt at said temperature is sufficiently low

for the solution to again be used for pickling purposes and in that the crystallized iron salt is removed from the solution.

In those acids or acid mixtures used when pickling iron, steel and other iron alloys the solubility of corresponding iron salts is dependent on the acid concentration and on the temperature. It has now further been found that presence of phosphoric acid has an influence on the solubility of the iron salts in a favourable direction in those concentration ranges being actual when regenerating the pickling solutions. By adjusting the acid concentration and temperatures to suitable values it is thus possible to precipitate iron salts from pickling solutions containing phosphoric acid in a manner that is favourable from an economic point of view and also from an energy point of view.

The reason why a phosphoric acid content of the magnitude set forth in the claims, that is up to 1 mole per litre, in this connection has such a favourable influence on the solubility conditions for iron is not quite made clear, but probably a displacement of the equilibria of the pickling solution will occur.

In accordance with the method of present invention, phosphoric acid containing pickling bath solutions are thus treated in three stages, whereby excess of dissolved iron is removed from the solution and the contents of acid and iron are re-set to values which are suitable for re-use as a pickling solution.

In a first stage there is added to the consumed pickling bath solutions a concentrated acid or an acid mixture containing one or both of these acids, whereat the composition of the solution is displaced towards the saturation value of corresponding iron salts at the temperature prevailing in the bath, which temperature, of course, can be slightly increased by the heat of solution as the acid is added. If the spent pickling bath solution does not contain any phosphoric acid also such acid is supplied to the solution in this stage,

suitably in the form of a mixture with sulphuric acid or hydrochloric acid. If phosphoric acid already is present in the spent pickling bath solution a minor amount phosphoric acid may be added to compensate for losses during the pickling. If the solution has a high iron content, the saturation value is exceeded after only a relatively small amount of acid is added, whereat precipitation of an anhydrous or hydrous iron salt commences. When the iron-content of the solution is low, however, the saturation value is not normally exceeded in this process stage. The amount of acid added in this stage is suitably adapted so as to at least substantially obtain the desired acid concentration in the pickling bath, and the desired maximum iron content can be adjusted with the cooling capacity available. Thus, in the next stage the pickling bath solution with the acid added thereto is cooled to a given temperature above or in the proximity of the ambient temperature, using some conventional method herefore. These methods, for example, may comprise conventional air cooling, water cooling or self-cooling processes. If precipitation has already commenced in the first process stage, it will continue during the cooling stage. Otherwise, the iron salts begin to precipitate when the saturation value is exceeded in said cooling stage. During the cooling stage, the iron content of the pickling bath decreases continuously with decreasing temperature. Since iron is precipitated as hydrous salts, the acid content of the solution increases indirectly during the cooling and iron-salt precipitation processes. Cooling in the second stage is continued to a temperature at which acid and iron contents of the pickling bath solution are suitable for re-use in pickling processes.

In a third and last stage of the method, the crystallized iron salt is separated from the bath solution. This separation can be effected by conventional methods, e.g. filtration, sedimentation and centrifugation. The residual solution freed of crystals is returned to the pickling operation. The acid in the solution is again consumed and iron is dissolved in said solution until said solution loses its pickling ability, whereupon it is again considered a consumed or spent solution and the aforedescribed regeneration stages are repeated.

The regeneration method can be carried out batchwise, whereat a major portion of a consumed pickling bath is removed and subjected to the aforedescribed stepwise treatment process. The regneration process can also be carried out semi-continuously or continuously, whereat minor portions of the bath or a continuous flow of bath solution are withdrawn and processed in accordance with the above. In this way variations in concentration during the pickling process are limited or completely eliminated.

By suitable selection of acid concentration and temperature, the described treatment cycle can be repeated without changing the quantity of bath solution. The amount of solution removed by crystallization can be compensated by the quantity of acid added. In practice, liquid is also lost by adhesion, vaporization and spillage. This loss must also be replaced by suitable additions to the bath.

Since the crystallization process is carried out while increasing the concentration in the bath, and displacing the equilibria by the presence of the phosphoric acid the temperature difference required for the desired degree of crystallization is lower than that required in known methods based on crystallization, and therefore the bath need not be cooled to temperatures beneath ambient temperature or exposed to a vacuum. The crystallization process can thus be carried out in a comparatively simpler apparatus with less cooling requirements than for prior art crystallization processes. The cooling therefore can readily be effected with air or available cooling water. The method is energy saving, and incurs lower investment costs and operational costs than hitherto known techniques.

By suitable selection of operating conditions, it is possible to control the actual pickling operation in an optimal manner, since both the concentration of acid and of iron in the pickling solution can be selected within reasonable limits already during the regeneration process. Thus, the acid content can be set at a value preferably within the range of 0.5-4 mol/l, whereat in the case

of sulphuric-acid based solutions there is suitably selected a content of 0.5-2.5 mol/l. The iron content, which in the consumed solution can be permitted to reach to 100 g/l or thereabove, can thus be lowered to a value which normally lies beneath 50 g/l. As will be understood, even lower contents can be obtained if desired, by a suitable combination of acid addition and cooling.

By the aforementioned selection of iron content it is possible in practice to utilize the well known phenomenom that a given content of iron in the pickling bath solution provides better pickling conditions than the normal starting position for pickling, when beginning with a freshly prepared acid solution which does not contain iron.

In practice suitable operating conditions are selected, such that both the iron concentration and the acid concentration are allowed to vary within the optimum range. In a continuous method, the concentrations of iron and acid may be selected so as to be practically constant at suitably selected operational conditions.

During a pickling operation components other than iron are also taken up in the pickling solution, e.g. alloying metals and oil. When practising the regenerating method according to the present invention, these components will be accumulated in the bath solution and may gradually build up to such concentrations as to disturb the pickling operation. In such a case, the pickling bath solution must be replaced or subjected to special purifying operations for removing these components.

The pickling and regenerating procedures are best illustrated on phase diagrams of actual systems, such as $FeSO_4$ - H_2SO_4 - H_2O or $FeCl_2$ - HCl - H_2O. One example of such a diagram is given in figure 1, in which the contents of $FeSO_4$ and H_2SO_4 present in aqueous solution in equilibrium with solid $FeSO_4$ are shown at different temperatures. Figure 2 shows a corresponding phase diagram for the system $FeCl_2$ -

HCl - H_2O. Figure 3 illustrates on a phase diagram over the system $FeSO_4$ - H_2SO_4 - H_2O a regenerating procedure both with and without presence of phosphoric acid for a sulphuric acid based pickling solution. Figure 4 illustrates in connection with a flow sheet showing the process of the present invention a mass and energy balance according to Example 3.

The invention will now further be illustrated by means of a number of non-limiting examples, in which "%" means "% by weight".

EXAMPLE 1

When pickling iron in a sulphuric acid solution, the acid concentration is supposed permitted to vary between about 16 and about 10 H_2SO_4. The pickling and regenerating procedure is illustrated by the diagram in Figure 3. Thus, the pickling starts at the point A in Figure 3, where the pickling solution contains 16 % H_2SO_4 and about 13 % $FeSO_4$. During the pickling process acid is consumed and iron sulphate simultaneously formed. When the acid concentration has fallen to about 10 % the pickling is broken off. The iron sulphate content is now 21 %, which can be seen from point B in the diagram.

The regenerating process is commenced by an addition of a 95 % sulphuric acid, whereby the H_2SO_4 content of the pickling solution increases, whereas the iron sulphate content decreases due to dilution. The acid supply is interrupted at point C^1 when the H_2SO_4 content has increased to a magnitude which is determined by the desired composition of the pickling solution being regenerated. The solution contains then about 13 % H_2SO_4 and 20 % $FeSO_4$.

Pickling with sulphuric acid is generally carried out at elevated temperatures, such as about 70°C. When sulphuric acid is added to the spent pickling solution a further temperature increase will occur. At the point C^1 the solution in the example has a temperature of about 77°C.

When the sulphuric acid supplied pickling solution is cooled, iron sulphate precipitation will commence when the temperature reaches a value corresponding to the solubility of the sulphate. In the present case sulphate will begin to precipitate in solid form at about 37°C.

During the crystallization process the content of $FeSO_4$ in the solution will decrease whereas the content of H_2SO_4 will decrease due to the fact that $FeSO_4 \cdot XH_2O$ is removed from the solution. Provided that the point C^1 has been suitable chosen the crystallization will be completed at the point A^1, at which point the solution again has the composition which is suitable for pickling. In this example the solution must be cooled to about 21°C to reach the desired composition.

EXAMPLE 2

The pickling procedure is performed following the same conditions as in Example 1, but the pickling solution is supplied with phosphoric acid so as to reach a content of 0.5 mol/l prior to the regenerating operation. The solubility of iron sulphate is hereby lowered, so that the 21°C equilibrium curve (corresponding to the final temperature in Example 1) lies about 5°C lower than in the system free from phosphoric acid. See Figure 3. Precipitation of iron phosphate will not occur at prevailing conditions. The pickling operation starts with a solution containing 17 % H_2SO_4 and 11.5 % $FeSO_4$ corresponding to point A^{11}. During the pickling operation the acid content decreases to about 10 %, while the iron sulphate content will increase to about 21 %, point B^{11}. Then sulphuric acid is supplied until point C^{11} is reached. At C^{11} the acid content is about 13.5 % and the iron sulphate content about 20 %.

During the cooling operation iron sulphate is precipitated from the solution, which will move the operation point from C^{11} back to A^{11}, which point corresponds to the initial composition of the pickling solution. Theoretically no phosphoric acid will be consumed during

the pickling-regeneration procedure irrespective of minor amounts which will adsorb on the pickling goods and also of spill and other inevitable losses. The pickling bath may thus theoretically be regenerated by addition of solely sulphuric acid, but, in practice, the solution must be replenished with sulphuric acid containing a phosphoric acid content adjusted to the circumstances.

EXAMPLE 3

Energy balances.

The benefit of utilizing a phosphoric acid containing pickling solution for the regenerating operation is set forth of the energy balances composing the Examples 1 and 2, respectively. In both cases 1000 m^2 steel sheet is pickled and the FeO scale removed corresponds to 40 g/m^2.

Provided that the process is performed using a heat exchange apparatus as indicated of the flow sheet in Figure 4 mass and enerby balances can be calculated as shown by the following table.

	Example 1	Example 2
Spent pickling solution		
amount in kg	1030	842
temperature ^oC	70	70
Subsequent to acid supply		
amount in kg	1070	882
temperature ^oC	77	77
Iron sulphate, kg	155	155
Regenerated pickling solution		
amount in kg	915	727
temperature ^oC	21	21
Energy demand, MJ		
final cooling-crystallization	89	75
heating to operation temp.	26	18
	115	93

Note: In practice it will be water losses in both cases by evaporation and so, which losses have been supposed to influence the mass and energy balance equally.

The presence of phosphoric acid will consequently result in a lowering of the amount pickling acid in operation and thereby also a reduction of the energy demand with almost 20 %, which is clearly shown of the figures corresponding to Example 2.

It will be evident that similar results as those obtained in the above examples may also be achieved also for hydrochloric acid pickling baths. The lowering of the solubility of $FeCl_2$ is here even more evident in this case and is furthermore dependent on the HCl concentration as is shown in the diagram of Figure 2 by the dotted line corresponding to a temperature of $20^{o}C$.

CLAIMS:

1. A method for regenerating pickling bath solutions based on sulphuric acid and/or hydrochloric acid and used for pickling iron, steel and other iron alloys by crystallization on cooling the solutions, characterized in that sulphuric acid or hydrochloric acid is added to the solution in a concentration higher than that of said solution in a quantity sufficient to substantially decrease the solubility of the iron salt corresponding to said acid at the temperature in question; in that a content of about 0.01-1 mole per litre of phosphoric acid is maintained in the solution; in that the solution is then cooled to a given temperature to crystallize out the iron salt, said temperature being so selected that the solubility of said iron salt at said temperature is sufficiently low for the solution to again be used for pickling purposes and in that the crystallized iron salt is removed from the solution.

2. A method according to claim 1, wherein the content of iron is decreased by crystallization to a value below 50 g/l, prior to the pickling bath solution being returned for pickling purposes.

3. A method according to claim 1 or 2, wherein the regenerating process is utilized together with a continuous pickling process, in which substantially constant pickling conditions are maintained.

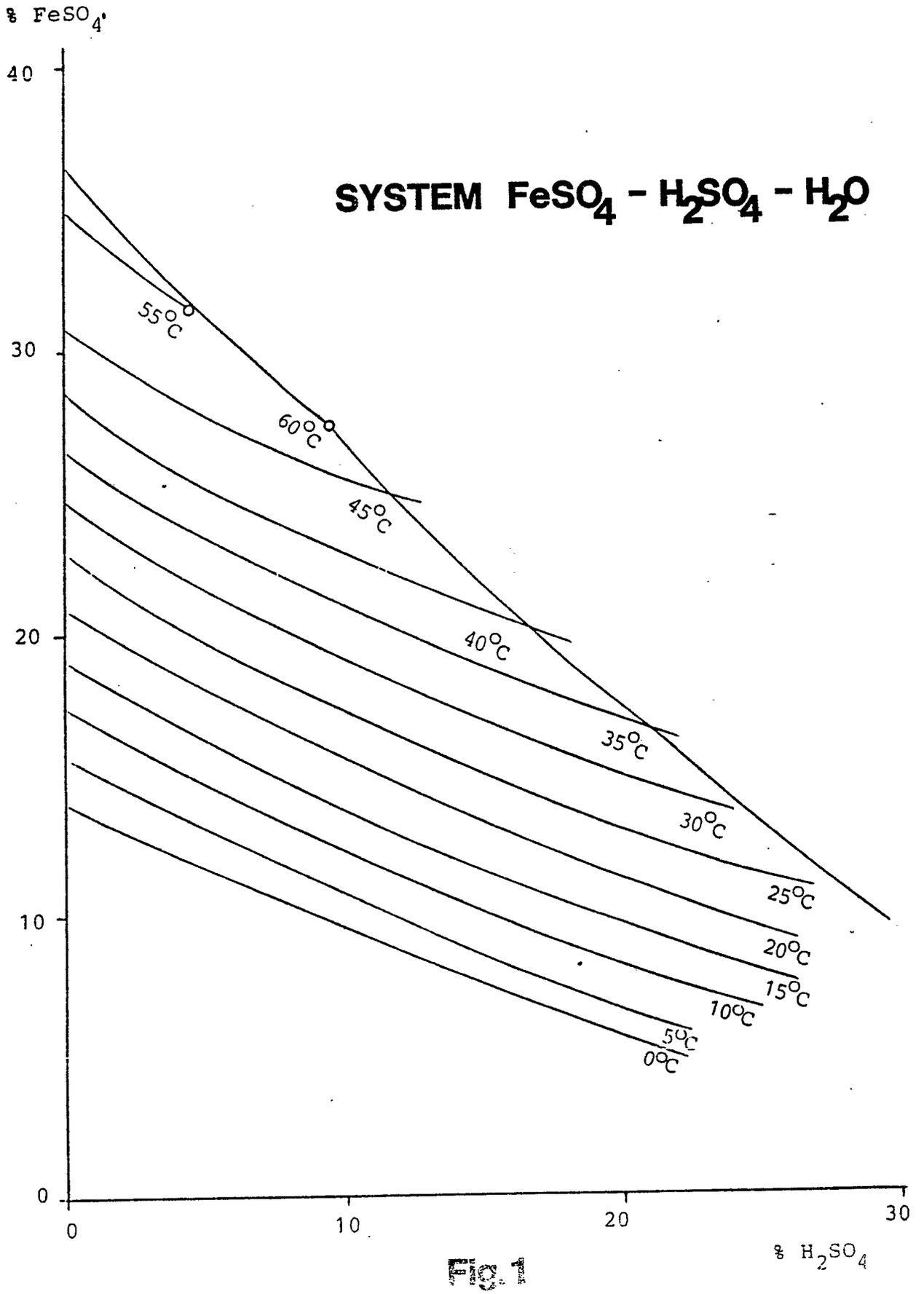

% FeSO4
40
30
20
10
0
SYSTEM FeSO4 - H2SO4 - H2O
55°C
60°C
45°C
40°C
35°C
30°C
25°C
20°C
15°C
10°C
5°C
0°C
0
10
20
30
% H2SO4

Fig. 1

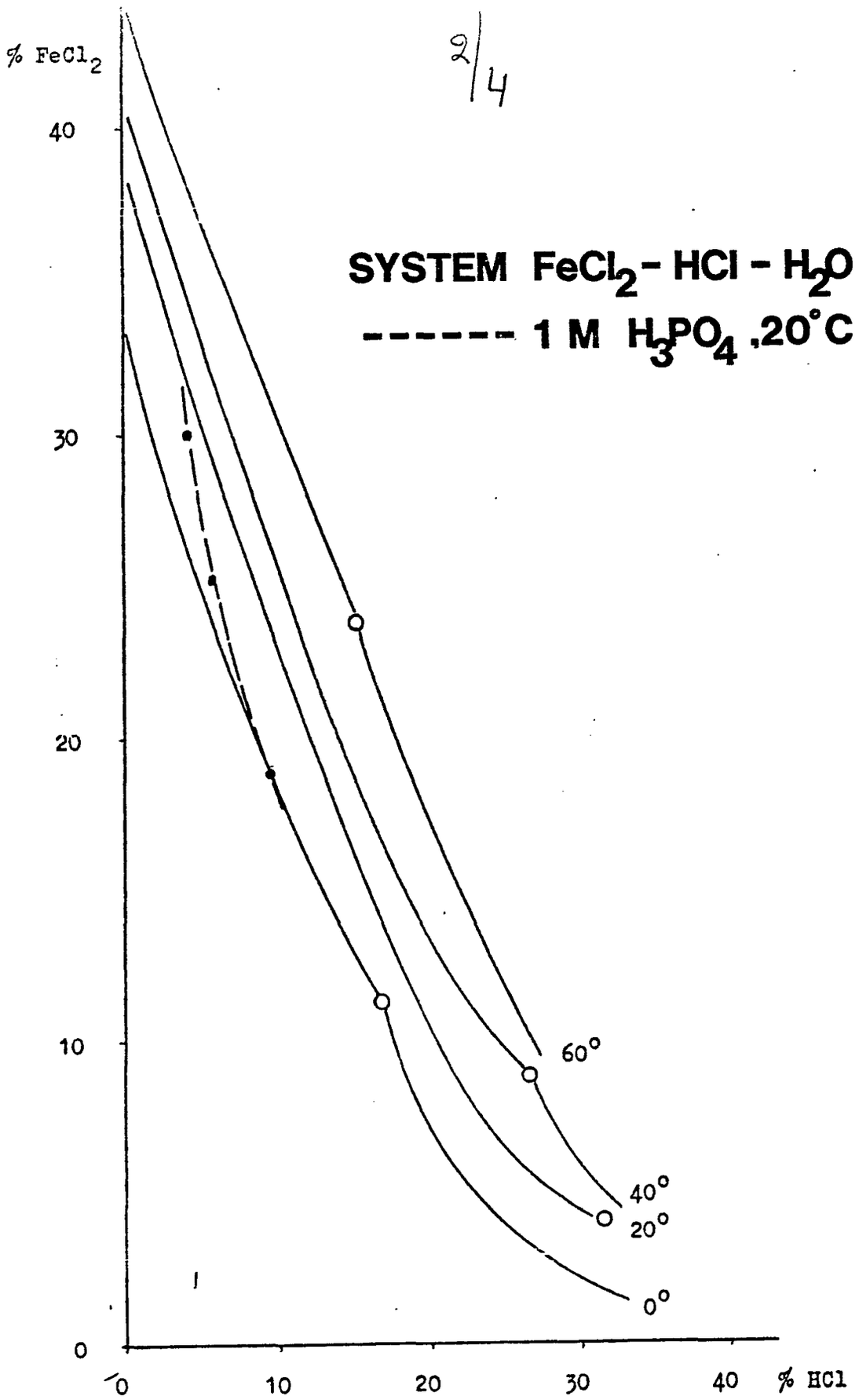
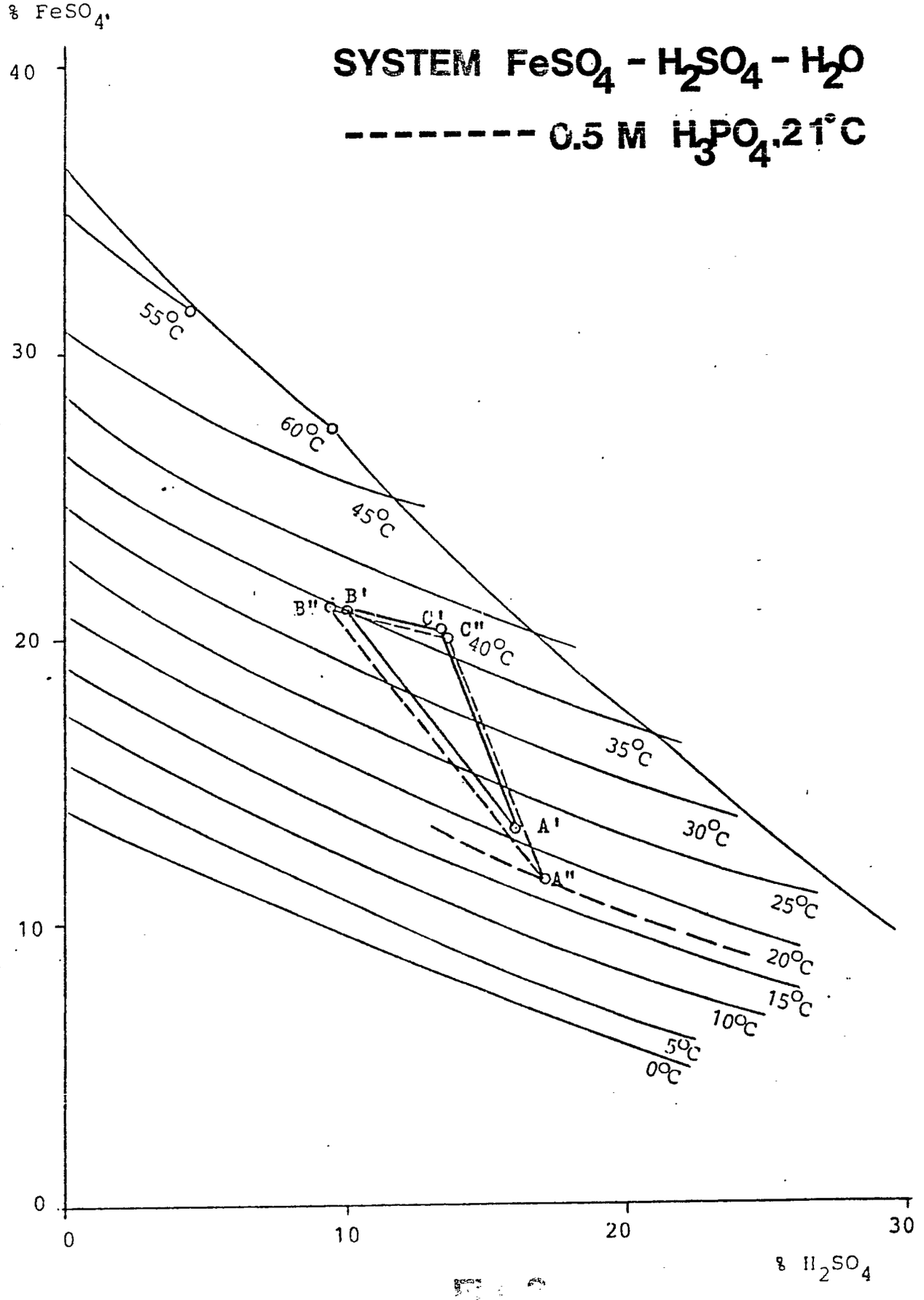

% FeCl2
40
30
20
10
0
SYSTEM FeCl2 - HCl - H2O
------ 1 M H3PO4 .20°C
60°
40°
20°
0°
1
0
10
20
30
40
% HCl

Fig. 2


% FeSO4
SYSTEM FeSO4 - H2SO4 - H2O
0.5 M H3PO4, 21°C
40
30
20
10
0
0
10
20
30
% H2SO4
55°C
60°C
45°C
40°C
35°C
30°C
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B'
B"
C'
C"

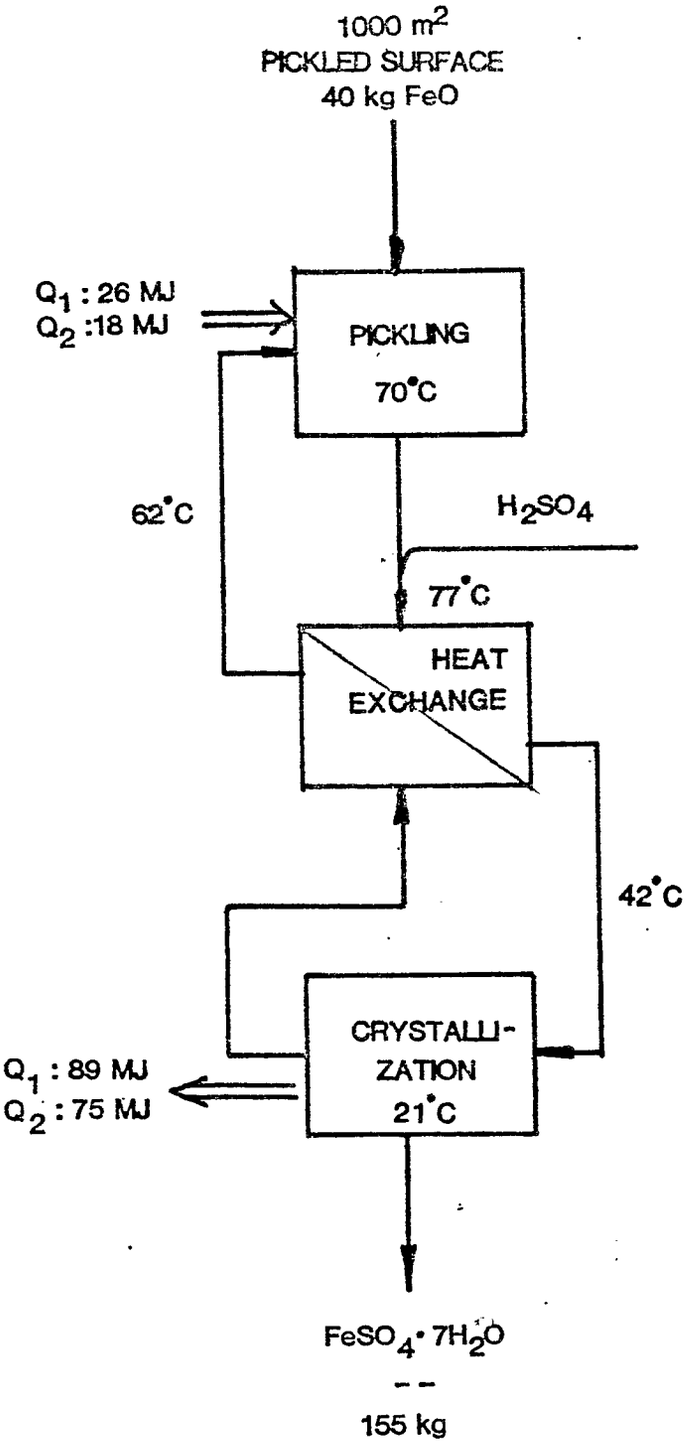
1000 m2
PICKLED SURFACE
40 kg FeO
Q1 : 26 MJ
Q2 :18 MJ
PICKLING
70°C
62°C
H2SO4
77°C
HEAT
EXCHANGE
42°C
CRYSTALLI-
ZATION
21°C
Q1 : 89 MJ
Q2 : 75 MJ
FeSO4 · 7H2O
155 kg

Fig. 4

0032

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The Netherlands

Re: Application No. 81850009.2 - Correction under rule 88

We apply for correction under Rule 88 of the above identi application. On Figure 4 a mistake has been done when pre paring the drawings. In the middle step is incorrectly written "LIQUID EXTRACTION" instead of "HEAT EXCHANGE". It will be evident from a study of the examples 1 through that the pickling acid in this second step is subjected t a cooling and thus the "heat exchange step" is obvious in this connection. We enclose 3 copies of an amended Figure to replace the originally filed one.

Stockholm, February 10, 1981

BOLIDEN AKTIEBOLAG

by: Björn-Eric Lundin

The correction is allowed.
The Hague, 13.04.81
Receiving Section.
R.K. VERHAGE

8

Encls.

Boliden Group activities: mining, smelting, chemicals, fertilizer, trading, know-how.
Group companies: Boliden Metall • Boliden Kemi • Supra • Boliden-Bergsöe • WP-System • Boliden-France • Boliden Canad
Associated companies: Norzink, Norway • Preussag-Boliden-Blei, West Germany • AB Svensk Alunskifferutveckling, ASA.

Mail address	Office address	Telephone No.	Cable address	Telex	Bank
					Banken

European Patent Office

EUROPEAN SEARCH REPORT

0032886

Application number

EP 81850009.2

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	AT - B - 247 104 (RUTHNER) + Claims + --	1
	DE - A - 2 209 954 (BABBEL) + Claims + --	1
	DE - A - 1 621 580 (GEWERKSCHAFT KERAMCHEMIE) + Claims + --	1
	DE - B - 1 124 781 (NIEDNER) + Claims + --	1
	GB - A - 1 271 891 (DAIDO CHEMICAL ENGINEERING CORPORATION) + Claims + ----	1

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

C 23 G 1/36

TECHNICAL FIELDS SEARCHED (Int. Cl.³)

C 23 G

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	19-03-1981	SLAMA

EPO Form 1503.1 06.78