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(71) Applicant *(for all designated States except US)*: KVAERNER PULPING TECHNOLOGIES AB [SE/SE]; Box 1033, S-615 15 Karlstad (SE).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: WENNBERG, Olle [SE/SE]; Vaktmästaregången 1, S-413 18 Göteborg (SE).

(74) Agent: BJÖRKMAN, Annika; Kvaerner Pulping Technologies AB, P.O. Box 1033, S-651 15 Karlstad (SE).

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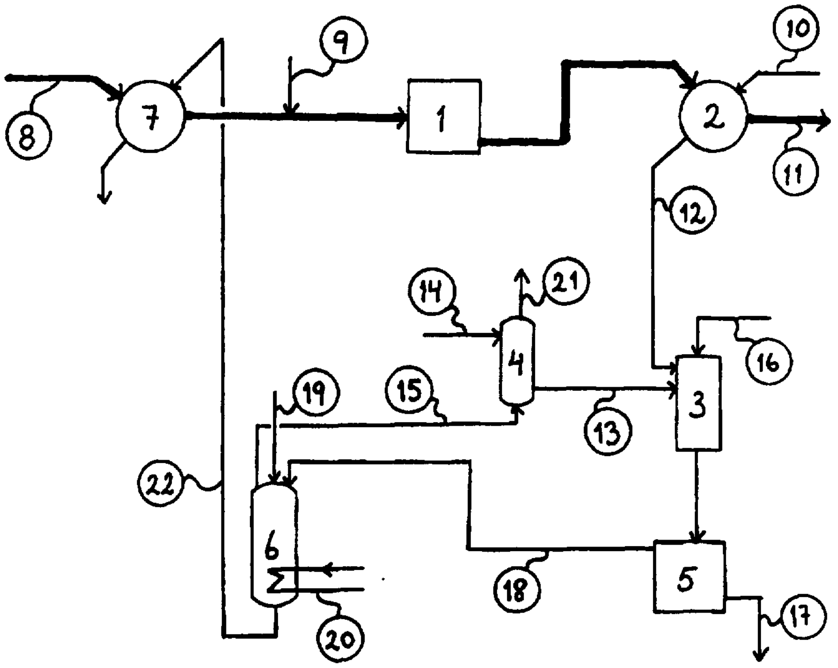
(54) Title: METHOD OF PRECIPITATING TRANSITION METALS AND ALKALINE EARTH METALS FROM BLEACH PLANT EFFLUENTS

(57) Abstract

Method of precipitating transition metals and alkaline earth metals out of bleaching department spent liquor from a chlorine-free bleaching process, in conjunction with producing lignocellulose-containing pulp, by means of supplying an alkaline liquid, which principally consists of green liquor, white liquor or a combination thereof, to the bleaching department spent liquor.



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Method of precipitating transition metals and alkaline earth metals from bleach plant effluents

TECHNICAL FIELD

The present invention relates to a method for precipitating unwanted positive ions of transition metals and alkaline earth metals from bleaching department spent liquor which is obtained when bleaching chemical paper pulp.

STATE OF THE ART AND PROBLEMS

Due to the increasing interest in the environment and understanding of the ecological cycle in nature, there is a great desire among both consumers and producers to decrease discharges of pollutants arising as a consequence of human activity.

Producers of pulp and paper have often been portrayed as villains in relation to the environment. However, vigorous efforts have been made in recent years to decrease the discharges from our pulp and paper mills and substantial progress has indeed been achieved.

One aim has been to create the closed pulp mill, that is to say a pulp mill from which there are no discharges since, as far as possible, chemicals which are present in the process are recovered and the spent liquors which have been formed are reused. A problem associated with such a closed pulp mill has been that of making it possible to return bleaching department spent liquors in countercurrent to the pulp in those cases where these spent liquors contain chlorine chemicals from a bleaching stage which is based on chlorine gas or chlorine dioxide. Successful attempts have been made to circumvent this problem by avoiding chlorine-containing chemicals and, instead, introducing hydrogen peroxide or ozone, for example, as bleaching chemicals. Another problem has been the risk of certain non-process elements, for example ions of transition metals, which are supplied to the process together with the raw wood material, for example, building up in high concentrations in the system when the spent liquors are returned. Such metal ions are often chelated, especially prior to a sensitive hydrogen peroxide stage where there is the risk that the peroxide will be decomposed by the metals. However, when filtrate from a washing stage which succeeds such a chelating stage is returned in countercurrent, there is the risk that the metal ions will be returned to the pulp by means of precipitating out on it.

An alternative to returning the bleaching department spent liquor in countercurrent to the pulp is to convey it, for example, to the mixing department, where it can be used as washing water, or to the soda smelt dissolver, where it can be used as make-up water. However, the quantity of spent liquor is usually too great for these uses, and, as a result, evaporation is necessary. A problem with this is that the spent liquor from a chlorine gas-free or chlorine dioxide-free bleaching department can contain large quantities of calcium which may precipitate out when the spent liquor is evaporated and form encrustations on the equipment.

In its Swedish Patent 417 114, Mo and Domsjö AB attempts to solve the problem of encrustation formation by adding a metal compound which is able to chelate encrustation-forming negative ions which are present in the process.

In Southern Pulp and Paper Manufacture, 40/1977, No. 8, pages 16-36, "Evaporator Scaling", Thomas M. Grace reported a method for "thermally deactivating" calcium in black liquor in order to avoid encrustation formation. This method consists in heat-treating the black liquor, to which calcium carbonate has been added to act as crystallization nuclei, at 150°C for 10 - 15 minutes. The theory behind the method is that the calcium in the black liquor is bound to organic substances, for example dissolved lignin and oxalate ions. During the heat treatment, the complex is broken down and the calcium ions precipitate out due to reaction with the carbonate ions which are naturally present in the black liquor. Calcium carbonate in solid (precipitated) form is not regarded as a cause of encrustation formation when liquid which contains such a precipitate is evaporated. Encrustations are only formed if the calcium carbonate precipitates out directly onto the hot heat-transfer surfaces of the evaporator.

This method has been found to be successful in preventing encrustation but cannot be directly applied to bleaching department spent liquors since the natural content of carbonate ions is low.

SOLUTION AND ADVANTAGES

By means of the present invention, it has been found to be possible, in a simple manner, to remove unwanted metals and/or render encrustation-forming calcium harmless in bleaching department spent liquor which is obtained when bleaching chemical paper pulp.

The concept of the devised method is to precipitate out transition metals and alkaline earth metals which are present in bleaching department spent liquor by adding an alkaline liquid which principally consists of green liquor and/or white liquor. The filtrate from a chelating stage, which makes use of EDTA, for example, for chelating transition metals which are harmful to the process, will contain the majority of these metals as well as alkaline earth metals such as calcium. This filtrate therefore represents a suitable point in the process for separating off these metals or rendering them harmless.

Anions such as OH^-, S^{2-} and CO_3^{2-} form difficultly soluble salts with the majority of transition and alkaline earth metals. Media in which such anions naturally occur, for example green liquor and white liquor, are present in the pulp mill. In accordance with the invention, these media are used for precipitating the metals.

According to one aspect of the invention, a method is provided for precipitating transition metals, in particular manganese, iron and copper, from the bleaching department spent liquor from a chlorine-free bleaching process so that these metals can be separated off by, for example, filtration or flotation. The spent liquor which has been purified in this way can then, if so desired, be returned in countercurrent to the pulp without the risk of metals precipitating out on the pulp.

The precipitation is effected by adding green liquor or white liquor to which carbon dioxide and/or hydrogen sulphide has preferably been supplied in order to obtain an increased content of carbonate and/or sulphide in the liquor. Lime sludge, burnt lime or slaked lime, for example, can also be added to the precipitation reactor in order to improve the precipitation conditions and adjust the pH. If the bleaching department spent liquor derives from a chelating stage or a washing stage subsequent to such a stage, it can be appropriate to disrupt the chelation of the metals by heat-treating the liquor at a temperature greater than 140°C, preferably at 150 - 170°C. The precipitate which forms is separated off and the filtrate is then treated with an acidic solution, preferably sulphuric acid, whereupon hydrogen sulphide and carbon dioxide are driven off, after which they are absorbed once again into green liquor or white liquor. Remaining gases which have not been absorbed are conveyed to a destruction point. Remaining hydrogen sulphide is expediently combusted to form sulphur dioxide or sulphur trioxide which can then replace some of the sulphuric acid which is used up. Precipitate which has been separated off is expediently destroyed in a bark boiler, for example, in connection with which it forms an ash which can be deposited.

An advantage of this embodiment of the

invention is that when the treated bleaching department spent liquor derives from a chelating stage, the chelating agent, for example EDTA, will to a large extent be regenerated. This chelating agent can then be reused when the filtrate is returned in countercurrent.

An additional advantage of this embodiment is that the addition of hydrogen sulphide and carbon dioxide has the effect of perhaps doubling the content of sulphide and carbonate in the green liquor, resulting in the quantity of green liquor which is required being about half the quantity which would otherwise have been required in order to bring about the desired precipitation. As a consequence, the quantity of sulphuric acid which is used up in neutralizing the green liquor will also be halved.

According to another aspect of the invention, a method is provided for precipitating alkaline earth metals, especially calcium, out of bleaching department spent liquor from a chlorine-free bleaching process so that there is no risk of these metals, since they are then already present in precipitated form, precipitating out during an evaporation process and forming encrustations on the equipment.

There can be an abundant quantity of calcium in bleaching department spent liquor from a chlorine-free bleaching process, and this calcium can often be present in dissolved form, especially if use is made of an acidic washing stage. If, for example, sulphuric acid is used, a solution of calcium sulphate is obtained even after neutralizing the spent liquor. While the solubility of calcium sulphate is relatively low, it is greater than that of calcium carbonate. While the presence of oxalate ions can result in difficultly soluble calcium oxalate being precipitated, the quantity of oxalate in the spent liquor is seldom sufficiently great to precipitate out any large quantity of calcium.

According to this embodiment of the invention, dissolved calcium is precipitated out by adding green liquor, resulting in the formation of calcium carbonate in solid form. The solubility of calcium carbonate is about 100 times lower than that of calcium sulphate. A relatively small quantity of green liquor can provide a substantial excess of carbonate ions, so that a large proportion of the calcium (> 90 %) is precipitated out. Some of the calcium can be bound to a chelating agent or, possibly, dissolved organic material, and it can, therefore, be expedient to disrupt the binding of the metals by heat-treating the liquor at a temperature greater than 140°C, preferably 150 - 170°C, prior to or in conjunction with the evaporation. In this embodiment, the precipitate which has been formed does not have to be separated off since it will constitute crystallization nuclei for ongoing precipitation and thereby assist in preventing precipitation on the heat-transfer surfaces of the evaporator. Where appropriate, additional lime can be added in the form of burnt lime or lime sludge in order to provide further crystallization nuclei. The bleaching department spent liquor can expediently be mixed with other cellulose spent liquor during the course of the evaporation.

An advantage of this embodiment of the invention is that the increased alkalinity due to the addition of green liquor provides favourable conditions for dissolving organic substances such as resins. The latter can otherwise smear heat surfaces or other apparatus parts.

BRIEF DESCRIPTION OF THE FIGURES

FIGURE 1 shows a preferred embodiment of the invention which is principally directed towards separating transition metals and alkaline earth metals out of bleaching department spent liquor from a chelating stage.

FIGURE 2 shows an alternative embodiment of the invention which is principally directed towards precipitating alkaline earth metals out of bleaching department spent liquor prior to evaporation.

DESCRIPTION OF THE FIGURES

As part of the bleaching sequence, the pulp stream 8 in Figure 1 passes through the washing stage 7. In a following stage 1, a chelating agent 9 (for example EDTA), which chelates the metal content, is supplied to the pulp. The chelating agent, which is soluble, is washed out of the pulp stream 11, together with the metal content, in a subsequent washing stage 2 which can, for example, utilize spent liquor from a hydrogen peroxide stage as the washing liquid 10. The chelating agent accompanies the filtrate 12 from the washing stage 2 to a precipitation reactor 3. A stream 13 is also supplied to this reactor; this stream 13 consists of green liquor or white liquor 14 which has been caused to absorb carbon dioxide and hydrogen sulphide 15 in a countercurrent column 4 for the purpose of increasing the content of carbonate and sulphide in the liquor. In the precipitation reactor 3, the different metals react with sulphide and carbonate to form a precipitate. For example, calcium carbonate and manganese sulphide are formed, both of which are very difficultly soluble. Lime sludge, or burnt or slaked lime 16 can be supplied to the reactor in order to adjust the pH and create more favourable precipitation conditions. The filtrate 12 is heat-treated (not shown in the figure) at a temperature of 150°C for the purpose of breaking the chelate bonds so that the metals are released and can precipitate out when the stream 13 is added to the reactor. After the precipitation, the liquid is filtered 5, with the precipitation products 17 being separated off. The filtrate 18, which now contains some carbonate and sulphide and has an elevated pH, is treated with sulphuric acid 19 in a column stripper 6, resulting in carbon dioxide and hydrogen sulphide 15 being driven off. The actual stripping can be effected, for example, using steam 20. The gases which have been driven off are returned to the countercurrent column 4 to be absorbed in green liquor or white liquor. The gases 21 which are not absorbed are conveyed onwards to a destruction point. In this connection, remaining hydrogen sulphide can be combusted to form sulphur dioxide or sulphur trioxide which can replace some of the sulphuric acid 19. Other adjustments aimed at decreasing the quantity of sulphuric acid required are also conceivable. After having been filtered 5 and treated with sulphuric acid 6, the spent liquor 22 from the column stripper is free of sulphide and carbonate. It additionally contains chelating agent which has been released from the metals and thereby regenerated. This spent liquor 22 is now returned, in countercurrent to the pulp, to washing stage 7. A large proportion of the liquid then accompanies the pulp to chelating stage 1, where the regenerated chelating agent is employed once again.

In an alternative embodiment of the invention, shown in Figure 2, green liquor 14 is supplied, in stage 31, to bleaching department spent liquor 12 from a chelating stage in a chlorine-free bleaching sequence. The liquor mixture is subsequently heat-treated in stage 32 at a temperature of 150°C for the purpose of releasing alkaline earth metals, especially calcium, from the chelation so that the metals can react with the green liquor and precipitate out, for example as calcium carbonate. The liquor 36, including the precipitate, is now conveyed to evaporation 33. There is no risk of the calcium, which has already precipitated out in the form of solid calcium carbonate, forming encrustations on the evaporation equipment and, instead, the calcium will serve as crystallization nuclei for ongoing precipitation in the solution. During the evaporation, it can also be expedient to supply other cellulose spent liquor which is to be evaporated.

After the evaporation sequence has been

completed in the desired number of effects, the spent liquor 37 can be supplied, for example, to the mixing department as washing water or to the soda smelt dissolver as make-up liquid.

EXPERIMENTS AND CALCULATIONS

When carrying out evaporation experiments on bleaching department spent liquors from chelating stages and hydrogen peroxide stages, it has been found that substantial quantities of precipitate are formed, which precipitate has the potential to precipitate out as encrustations on heat surfaces. Analysis of this precipitate shows that approximately one tenth of it consists of calcium which, as calcium sulphate and calcium oxalate, corresponds to one third by weight of the precipitate.

Precipitation experiments were carried out at a temperature of 90°C, with green liquor being added to solutions of spent liquor from chelating stages and hydrogen peroxide stages. These concentrated solutions had been diluted beforehand to COD contents of 2, 5, 10 and 20 g/l. Increasingly large quantities of green liquor were added to these solutions and, after each addition, a sample was taken of the solution, which was filtered. The quantity of soluble calcium which remained in the sample filtrate was then determined.

The best results were achieved with solutions of low COD content (2 g of COD/l). This COD content corresponds approximately to the content which is obtained in a bleaching department which is totally chlorine-free. Approximately 90 % of the calcium was precipitated out by adding only 20 ml of green liquor per litre of bleaching department spent liquor solution. Further addition of green liquor resulted in only a small decrease in the quantity of calcium remaining in the filtrate.

The experiments clearly demonstrate that adding green liquor to bleaching department spent liquor from both chelating stages and hydrogen peroxide stages can promote substantial precipitation of calcium. The effect on transition metals such as manganese, for example, is similar.

If green liquor is used in the embodiment according to Figure 1, 0.2 m^3 of green liquor would be required per tonne of pulp if the quantity of spent liquor from the chelating stage is 10 m^3 per tonne of pulp. This quantity of green liquor would then require approximately 40 kg of sulphuric acid per tonne of pulp for its neutralization if special adjustments are not made to decrease the quantity required.

The embodiments shown in Figures 1 and 2 and in the experimental description are preferred embodiments. However, the invention is not limited to these embodiments and can be varied within the scope of the subsequent patent claims.

For example, it will be readily evident to the person skilled in the art that the concept of the invention can be used for spent liquor from another stage in the bleaching department sequence, just as the disposition of the apparatus can be different. The actual reason for wishing to precipitate out transition metals or alkaline earth metals can also vary.

PATENT CLAIMS

1. Method of precipitating transition metals and/or alkaline earth metals out of bleaching department spent liquor from a chlorine-free bleaching process, in conjunction with producing lignocellulose-containing pulp, by means of supplying an alkaline liquid (14) to the bleaching department spent liquor (12), characterized in that the alkaline liquid principally consists of green liquor, white liquor or a combination thereof.

2. Method according to Patent Claim 1, characterized in that the bleaching department spent liquor (12) is derived from a stage in the bleaching department sequence for chelating metals or from a stage for bleaching with hydrogen peroxide or from a washing stage immediately downstream of such a chelating stage or hydrogen peroxide stage.

3. Method according to Patent Claim 1, characterized in that the metals which are precipitated out are calcium, manganese, iron and copper.

4. Method according to Patent Claim 1, characterized in that the sulphide and carbonate content in the alkaline liquid is increased before it is supplied to the bleaching department spent liquor.

5. Method according to Patent Claim 4, characterized in that the sulphide and carbonate content in the alkaline liquid is increased by supplying carbon dioxide and hydrogen sulphide (15) to the liquid.

6. Method according to Patent Claim 1, characterized in that the precipitate

which has been obtained is preferably separated from the bleaching department spent liquor by means of filtration (5) or flotation.

7. Method according to Patent Claim 1, characterized in that the bleaching department spent liquor is evaporated (33) with the precipitate which has been obtained remaining in the spent liquor.

8. Method according to Patent Claim 2 or 7, characterized in that the bleaching department spent liquor is heat-treated at a temperature greater than 140°C, preferably at 150 - 170°C.

9. Method according to Patent Claim 1 or 8, characterized in that other cellulose spent liquors are supplied to the bleaching department spent liquor and in that the spent liquor is subsequently or simultaneously evaporated.

10. Method according to Patent Claim 4, characterized in that carbon dioxide and hydrogen sulphide are driven off (6) from the bleaching department spent liquor, after the precipitation, by means of the spent liquor being treated with an acidic solution, preferably sulphuric acid (19).

AMENDED CLAIMS

[received by the International Bureau on 11 March 1996 (11.03.96);
original claims 1-10 replaced by amended claims 1-9 (2 pages)]

1. Method of precipitating transition metals and/or alkaline earth metals out of bleaching department spent liquor from a chlorine-free bleaching process, in conjunction with producing lignocellulose-containing pulp, by means of supplying an alkaline liquid (14), principally consisting of green liquor, white liquor or a combination thereof to the bleaching department spent liquor (12), characterized in that the bleaching department spent liquor subsequently is evaporated (33) with the precipitate which has been obtained remaining in the spent liquor.

2. Method according to Patent Claim 1, characterized in that the bleaching department spent liquor (12) is derived from a stage in the bleaching department sequence for chelating metals or from a stage for bleaching with hydrogen peroxide or from a washing stage immediately downstream of such a chelating stage or hydrogen peroxide stage.

3. Method according to Patent Claim 1, characterized in that the metals which are precipitated out are calcium, manganese, iron and copper.

4. Method according to Patent Claim 1, characterized in that the sulphide and carbonate content in the alkaline liquid is increased before it is supplied to the bleaching department spent liquor.

5. Method according to Patent Claim 4, characterized in that the sulphide and carbonate content in the alkaline liquid is increased by supplying carbon dioxide and hydrogen sulphide (15) to the liquid.

6. Method according to Patent Claim 1, characterized in that the precipitate which has been obtained is preferably separated from the bleaching department spent liquor by means of filtration (5) or flotation.

7. Method according to Patent Claim 1 or 2, characterized in that the bleaching department spent liquor is heat-treated at a temperature greater than 140°C, preferably at 150 - 170°C.

8. Method according to Patent Claim 1 or 7, characterized in that other cellulose spent liquors are supplied to the bleaching department spent liquor and in that the spent liquor is subsequently or simultaneously evaporated.

9. Method according to Patent Claim 4, characterized in that carbon dioxide and hydrogen sulphide are driven off (6) from the bleaching department spent liquor, after the precipitation, by means of the spent liquor being treated with an acidic solution, preferably sulphuric acid (19).

Fig 1

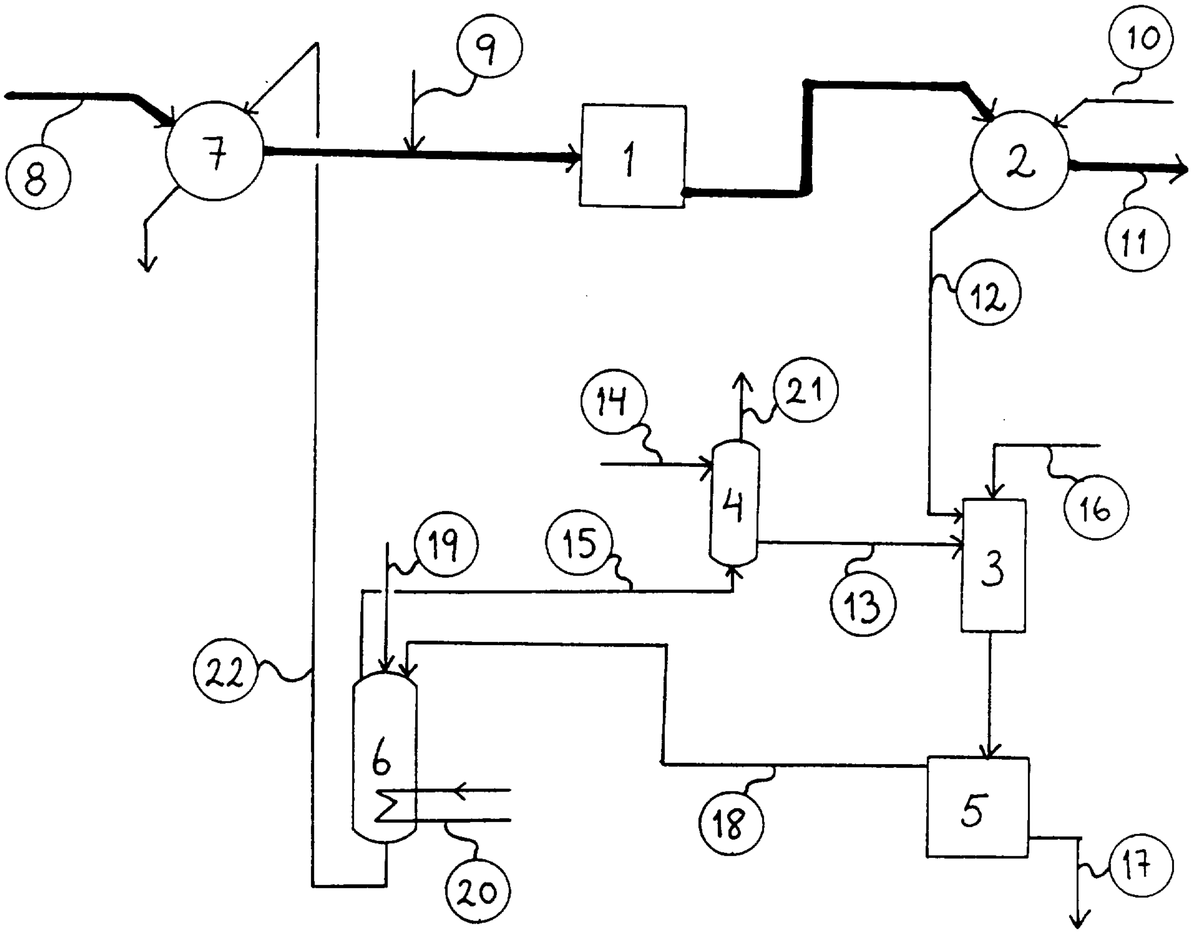
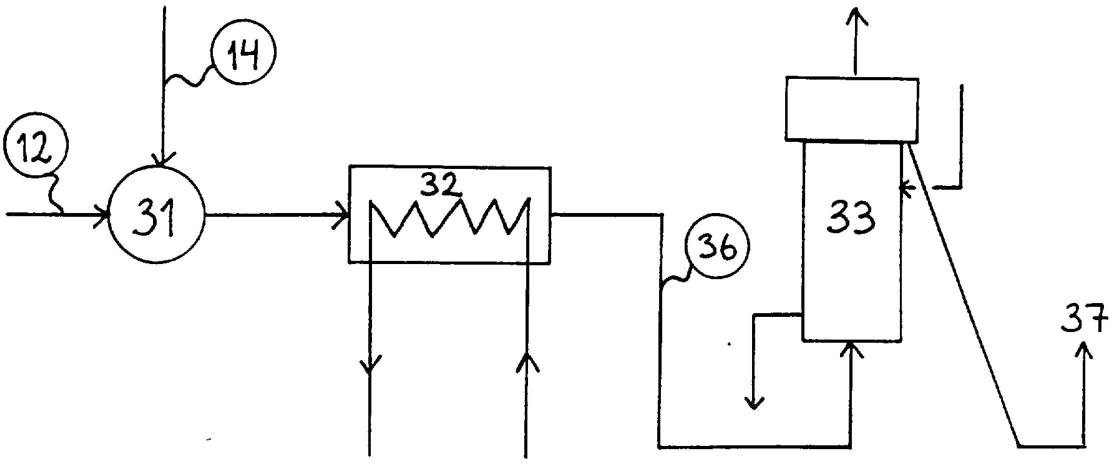


Fig 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 95/01281

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D21C 11/00, D21C 9/10
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)

IPC6: D21C

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

SE,DK,FI,NO classes as above

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9423122 A1 (SUNDS DEFIBRATOR INDUSTRIES AB), 13 October 1994 (13.10.94), page 1, line 5 - line 10; page 2, line 26 - page 3, line 19	1,2,3,6,9
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X	WO 9421857 A1 (KAMYR, INC.), 29 Sept 1994 (29.09.94), page 1, line 12 - line 24, figure 1, claims 41,42,43,46,48,49,50,51,53	1-3,6,9
A	page 8, line 14 - line 18	8
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P,A	WO 9504188 A1 (KVAERNER PULPING TECHNOLOGIES AB), 9 February 1995 (09.02.95), figure 1, abstract	1,8,9
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search 2 February 1996	Date of mailing of the international search report 07 -02- 1996
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 95/01281

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SOUTHERN PULP AND PAPER MANUFACTURER, Volume 40, No 8, August 1977, Grace T.M., "Evaporator Scaling", page 16 - page 23, cited in the application --	8
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INTERNATIONAL SEARCH REPORT

Information on patent family members

05/01/96

International application No.

PCT/SE 95/01281

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A1- 9423122	13/10/94	NONE	
WO-A1- 9421857	29/09/94	NONE	
WO-A1- 9504188	09/02/95	NONE	
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		CA-A- 1120211	23/03/82
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