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DECISION
of 20 September 2001

Case Number: T 0453/99 - 3.3.5

Application Number: 91308493.5

Publication Number: 0513454

IPC: C02F 11/08

Language of the proceedings: EN

Title of invention:
Caustic sulfide wet oxidation process

Patentee:
U.S. FILTER/ZIMPRO, INC.

Opponent:
Nippon Petrochemical Co. Ltd.

Headword:
Wet oxidation/U.S. FILTER

Relevant legal provisions:
EPC Art. 56

Keyword:
"Inventive step - no, obvious solution of a known problem."

Decisions cited:
-

Catchword:
-

Case Number: T 0453/99 - 3.3.5

DECISION
of the Technical Board of Appeal 3.3.5
of 20 September 2001

Appellant:
(Opponent)

Nippon Petrochemical Co. Ltd.
3-1, 1-chome, Uchisaiwaicho, Chiyoda-ku
Tokyo (JP)

Representative:

Schübel-Hopf, Ursula
Strehl Schübel-Hopf & Partner
Patentanwälte
Postfach 22 14 55
D-80504 München (DE)

Respondent:
(Proprietor of the patent)

U.S. FILTER/ZIMPRO, INC.
10 Technology drive
Lowell, Massachussets 01851 (US)

Representative:

Goodanew, Martin Eric
MATHISEN, MACARA & CO.
The Coach House
6-8 Swakeleys Road
Ickenham
Uxbridge UB10 8BZ (GB)

Decision under appeal: **Decision of the Opposition Division of the European Patent Office posted 18 February 1999 rejecting the opposition filed against European patent No. 0 513 454 pursuant to Article 102(2) EPC.**

Composition of the Board:

Chairman: R. K. Spangenberg
Members: G. J. Wassenaar
J. C. M. De Preter

Summary of Facts and Submissions

I. The appeal is from the decision of the Opposition Division to reject the opposition against European patent No. 0 513 454. The patent was based on the European patent application No. 91308493.5. The patent was granted with 6 claims. Claim 1 thereof reads as follows:

"A process for treatment of a caustic sulfide liquor by wet oxidation in a nickel-based alloy system comprising the steps:

a) analyzing the caustic sulfide liquor to determine the initial concentrations therein of total alkalinity, total sulfides, mercaptans, COD, thiosulfate, total carbonate and pH, and determining from the results of this analysis the amount of nonsulfidic alkalinity which would be consumed by said liquor upon wet oxidation treatment and the amount of nonsulfidic alkalinity initially available in said liquor;

b) adding a sufficient amount of additional nonsulfidic alkalinity to said caustic sulfide liquor such that the sum of the initially available nonsulfidic alkalinity and said additional nonsulfidic alkalinity exceeds the amount of nonsulfidic alkalinity which will be consumed upon wet oxidation treatment as determined in step a; and

c) carrying out said treatment process of wet oxidation upon said caustic sulfide liquor within said nickel-based alloy system to destroy sulfides and mercaptans and produce a treated liquor containing excess nonsulfidic alkalinity."

II. In the decision, inter alia, the following prior art documents were considered:

D1: JP-B-49-33845,

D3: JP-A-54-108462,

D4: JP-A-52-150778,

D6: "Chemical Analysis of Industrial Water", James W. McCoy (1969), pages 125 to 153,

D7: US-A-4 350 599.

The opposition grounds were lack of novelty and lack of inventive step (Article 100(a) EPC). The Opposition Division held that D1 represented the closest prior art. The process of granted claim 1 would differ therefrom in that

- the oxidation treatment took place in a nickel-based alloy system,

- the caustic sulfide liquor was not only analysed for pH, thiosulfate and COD as disclosed in D1 but also for the initial concentrations of total alkalinity, total sulfides, mercaptans and total carbonate, and

- on the basis of this analysis the amount of nonsulfidic alkalinity, which would be consumed by said liquor upon oxidation treatment, and the amount of nonsulfidic alkalinity initially available were determined in order to determine the necessary amount of additional nonsulfidic alkalinity.

It was argued that the corrosion problems in D1 were not comparable to those of the patent in suit. The waste liquor in D1 was less caustic, different bases were added and the equipment used in D1 was probably made of stainless steel. The process of the patent in suit could achieve a more accurate calculation of the necessary amount of base to be added. The said differences made it possible to safely treat high alkaline waste waters and involved an inventive step. The other documents were considered not to add anything to the teaching of D1.

III. In the statement of the grounds of appeal, the appellant(opponent) maintained the objections raised before the first instance. Novelty of claim 1 was attacked on the basis of D1 . An inventive step of the processes according to claim 1 was denied in view of D1 in combination with D6 . During oral proceedings, which were held on 20 September 2001, novelty was no longer disputed. With respect to inventive step further reference was made to D7.

The appellant's arguments may be summarized as follows:

As evidenced by D7, it was common general knowledge in the art of wet oxidation treatment of caustic sulfide liquor to use a nickel-based alloy reactor system if the pH of the liquor was high. D7 also showed that it was common general knowledge that acid was produced during the oxidation treatment and that under acid conditions the reactor system would be corroded. D1 specifically disclosed the addition of an ammonia containing gas liquor to a caustic sulfide waste liquor in an amount necessary for neutralisation, which is calculated from the amount of ammonia contained in the gas liquor and the concentrations of thiosulfates and sulfur in the waste liquor. The other components mentioned in claim 1 needed not to be determined if it was known beforehand that the waste water could not contain them. The waste liquors treated according to the examples did not contain all the components mentioned in claim 1 so that the method according to claim 1 covered also waste liquors which did not contain all the components mentioned therein. No technical problem beyond D1 was solved.

IV. During oral proceedings the Board drew the parties' attention also to D3 and D4, both concerning a wet oxidation treatment of a caustic sulfide liquor under such conditions that the pH was reduced but remained basic.

V. The respondent's (proprietor) arguments may be summarized as follows:

A nickel-based alloy system was only used for the treatment of a highly alkaline caustic liquor. At the pH range from 8 to 10, as mentioned in D1, stainless steel was normally used. According to D1 ammonia gas liquor was added to the waste liquor for neutralizing the acid formed during the wet oxidation. The examples of D1 showed that after the treatment the pH was higher so that the amount of alkalinity already present in the waste liquor was not taken into consideration. Both the waste liquor and the neutralizing agent according to D1 were different from those used in the patent in suit. There was no reason for the skilled person to analyse the waste liquor of D1 for total alkalinity, total sulfides, mercaptans and total carbonates. The fact that D6 disclosed how to measure the concentrations of all possible components did not make it obvious to do so. D3 and D4 related to different processes. According to D3 a copper catalyst was added and according to D4 a caustic hydrogen peroxide was used for the oxidation of the waste liquor. Although the object of the invention was to prevent corrosion, it had the additional advantage that conditions could be so chosen that the treated liquor was less alkaline, requiring less acid for neutralisation prior to discharge to the environment. The skilled person was not motivated to determine each potentially acidic component or each neutralizing agent that might also be present in the waste liquor and to take it into account for determining the amount of neutralizing agent to be added to prevent corrosion.

VI. The appellant requested that the decision under appeal be set aside and that the European patent No. 513 454 be revoked.

The respondent requested that the appeal be dismissed.

Reasons for the Decision

1. Novelty was no longer disputed during the oral proceedings. From the following analysis of inventive step it is evident that the subject-matter of claim is new.

2. According to claim 1 the caustic sulfide liquor is treated in a reactor made of a nickel-based alloy. Such an alloy is much more expensive than conventional

stainless steel and is only used if the liquor has a high pH value. The technical problems related to the treatment of high caustic liquors are generally different from those encountered in low caustic liquors. The treatment of a high caustic liquor requiring the use of a nickel-based alloy has been disclosed in D7, but not in D1. The Board, therefore, holds that D7 is more suitable as a starting point for an inventive step analysis than D1.

3. D7 discloses that it is known in the art to treat sulfide-containing caustic waste liquors of a pH of about 13 effectively by wet oxidation for almost complete destruction of the pollutants, whereby sulfides are oxidized to sulfates and the organic substances are primarily converted to carbon dioxide and water. It further discloses that the high preheat and reaction temperatures require special construction materials of the wet oxidation system to prevent corrosion, and that high nickel alloys such as Incoloy 800 are resistant to alkali at higher temperatures but are expensive (column 1, lines 6 to 15 and lines 38 to 43). Starting from this prior art teaching, the problem underlying the invention can be seen in preventing corrosion of a nickel-based alloy reactor system in the treatment of a caustic sulfide liquor by wet oxidation. The patent in suit proposes to solve this problem by steps (a) and(b) of claim 1, thereby ensuring that during the wet oxidation treatment the liquor does not become acidic. It is common general knowledge that nickel-based alloys, like all alloys based on a metal which are more electronegative than hydrogen, are not resistant to acids. Since it is evident that by the method according to claim 1 the formation of acid is prevented the Board

is satisfied that the process according to claim 1 actually solves the above-mentioned problem.

4. D7 does not specifically relate to the problem of avoiding corrosion in a nickel-based alloy system but is directed to operational conditions which make it possible to perform the process safely in a stainless steel reactor. To this end D7 proposes to add an acid or carbon dioxide to the caustic waste liquor in order to reduce the pH of the liquor below 11.0 but preferably not below 7 and to contact the additional incoming raw caustic waste liquor with a carbon dioxide containing gas to neutralize the caustic waste. The use of carbon dioxide ensures that the pH remains on the alkaline side in view of the alkali metal carbonate content of the solution (column 2, lines 16 to 57). With respect to a nickel alloy system it is observed in D7 that preheating of the feed must be performed in the presence of oxygen because of high corrosion rates under oxygen deficient conditions (column 1, lines 41 to 47 and column 5, lines 43 to 49). D7 does not disclose additional measures to ensure that the solution does not turn acidic during the wet oxidation treatment. For waste liquors with a high amount of hydroxide and a relatively low amount of sulfur compounds as used in Example 1 of D7 the liquor will remain alkaline during the wet oxidation treatment without adding additional alkali. The skilled person will realize that only for waste liquors having a relatively low amount of hydroxide and a high amount of acid forming pollutants, such as sulfides and organic substances, measures must be taken to prevent the treated liquor from becoming strongly acidic. In such a situation the skilled person will look into other documents concerning wet oxidation treatment and

consider the solutions for this problem given therein.

5. The parties agreed that the skilled person would have considered D1. This document, a patent publication of the Japanese Patent Office was submitted by the appellant together with an English translation thereof. The translation was not contested by the respondent (the following references to D1 relate in fact to the English translation thereof). D1 relates to a process for treatment of waste liquor from a coke oven plant and discloses that such a waste liquor contains sulfur and sulfur compounds which, when subjected to an oxidation treatment, are easily oxidized to produce sulfuric acid so that the liquor becomes strongly acidic and that this is a serious problem for the material of the apparatus (paragraph bridging pages 3 and 4). In order to avoid the formation of free acid D1 proposes to add an amount of ammonia containing gas liquor necessary for neutralization which is calculated from the amount of ammonia contained in the gas liquor and the concentrations of thiosulfates and sulfur in the waste liquor, whereby the pH can be maintained at a suitable value for release of the treated liquor and the material of the treating apparatus (paragraph bridging pages 4 and 5). The only acid forming pollutants identified in the examples are thiocyanate and thiosulfate.

However, if a skilled person has to solve the related problem of treating a waste liquor in which other acid forming substances were also present, such as sulfides and mercaptans, it is within the ordinary skills of such person to take their concentration also into account for calculating the necessary amount of gas liquor to be added. It is also routine to determine the pH and COD values of the liquor (D1, Tables and D7, Example 1). In D1 an ammonia containing gas liquor is added as neutralizing agent because it is available as a waste product on the coke oven plant. Other neutralizing agents such as sodium hydroxide and sodium carbonate were also contemplated but rejected for cost reasons (page 4, lines 6 to 11). In other gas washing processes, such as the washing of cracked gas from a naphtha cracker, sodium hydroxide solutions are used; see D4 (English translation, Example 2). In such a process, where sodium hydroxide is available on the plant in large quantities , a skilled person would certainly consider the use of sodium hydroxide as a neutralizing agent if necessary. Crack gases always contain some carbon dioxide so that the spent liquor will also contain sodium carbonate and, depending on the pH, sodium bicarbonate. It is then also obvious not only to determine the amount of sodium hydroxide in the liquor but also the amounts of sodium carbonate and bicarbonate. From table 1 of D4 it is apparent that in practice the concentrations of all the components mentioned in step (a) of present claim 1 are determined if they can be expected to be present. It is true that the process according to D4 is a wet oxidation process using hydrogen peroxide as an oxidant and not a high pressure wet oxidation process with gaseous oxygen. Present claim 1 seems, however, also to cover the oxidation treatment according to D4. But even if treatment by wet oxidation according to claim 1 would exclude the hydrogen peroxide treatment according to D4, the fact remains that D4 shows that in the art of wet oxidation of caustic sulfide liquors normally the concentrations of all caustic and sulfur containing compounds are determined.

6. The corrosion problem by acid attack which might occur during the wet oxidation of a caustic sulfide liquor is also discussed in D3 (last paragraph of page 3 of the English translation). D3 proposes to adjust the pH of the waste liquor so that after treatment it will remain neutral to alkaline even after a free acid has been produced by the oxidation (page 5, second full paragraph). This teaching is not invalidated by the fact that D3 also proposes to add a copper catalyst solution. Thus not only the problem of corrosion risk during the wet oxidation treatment was known in the art but also the solution of this problem by adjusting the pH through additional alkali. It is obvious for a skilled person not to add more alkali than necessary for neutralization of the acid formed during the wet oxidation treatment because, before the treated liquor can be discharged in the environment, any surplus of alkali must be neutralized (D3, page 5, second full paragraph). In order to know whether additional alkali is necessary and, if so, how much is necessary to secure alkaline conditions without making it unnecessarily caustic, the initial concentrations of all the relevant components must be determined.

7. The chemical analysis of caustic sulfide liquors is disclosed in D6. For the estimation of hydroxide, sulfide, mercaptan and carbonate, D6 teaches to determine the concentrations of total alkalinity, total sulfide, mercaptan and total carbonate. With the knowledge of pH it is then possible to accurately determine the concentrations of hydroxide, carbonate, bicarbonate, sulfide, bisulfide, mercaptan (pages 139 to 151). If thiosulfates and organics may also be present it is obvious to determine the concentrations of these compounds because the skilled person knows

that these compounds produce alkali-consuming acids by oxidation. The determination of thiosulfate in the presence of sulfide is done by a routine analysis; see D6, pages 134 to 137. The amount of organics follows from the standard determination of the COD value after subtracting the inorganic oxygen consuming species.

8. From the above it follows that the skilled person trying to prevent corrosion was aware of the need to add an additional amount of alkali to a caustic sulfide liquor if the amount of non-sulfidic alkali in the liquor was not sufficient to neutralize the acid formed during wet oxidation. In order to determine the necessary amount of additional alkali he will, as a matter of routine, analyse the liquor by standard methods and calculate how much acid will be produced and how much alkali remains available for neutralization. Nothing more is proposed by present claim 1.

9. The respondent's argument that following the teaching of D1 the skilled person would not take into account the non-sulfidic alkali present in the caustic sulfide liquor, is not convincing. In D1 the waste liquor treated in the examples have a low pH (<9) and a high content of acid forming, sulphur containing, substances such as thiocyanate and thiosulfate. In these circumstances the amount of non-sulfidic alkali must have been low so that there was no need to determine it and to take it into account for calculating the amount of additional alkali. Therefore, D1 does not show that in the case of strong caustic waste liquors having a high pH (about 13), such as disclosed in D3, D4 and D7, for which it is not clear, without complete analysis of the liquor, whether additional alkali is required for

neutralization or not, the skilled person would not have considered to determine the available non-sulfidic alkali and take it into account for calculating the required amount of additional alkali.

10. For these reasons the Board holds that the process according to present claim 1 is the result of obvious considerations which a skilled person, guided by the prior art, would apply for solving the above-mentioned problem . Such a method, requiring not more than basic chemical skills, therefore does not involve an inventive step.

Order

For these reasons it is decided that:

1. The decision under appeal is set aside.

2. The patent is revoked.

The Registrar:	The Chairman:
Ch. Eickhoff	R. Spangenberg