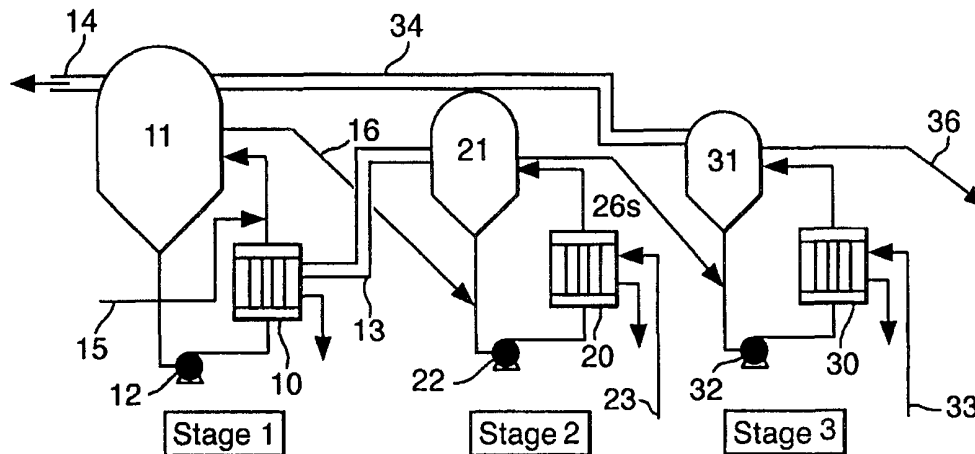




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(54) Title: PROCESS FOR THE CONCENTRATION OF DILUTE SULPHURIC ACID SOLUTIONS



(57) Abstract

In a process for the concentration of dilute sulphuric acid containing metal salts using a multistage heat exchanger vacuum evaporator system, contamination of the system by metal salt deposition can be reduced by a) feeding part of the acid to the first stage of the multistage system operating at an acid concentration of less than 30 %; b) feeding the remainder of the dilute acid to a separate heat exchanger vacuum evaporator using waste heat as the heating medium and operating at an acid concentration of greater than 40 %; c) feeding the acid from steps (a) and (b) to the second stage of the multistage system operating at a concentration of greater than 50 % and recycling steam generated in the evaporator as the heating medium for the first stage, and; d) feeding the acid from the second stage to such subsequent steps as are necessary to produce the required final acid concentration.

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**PROCESS FOR THE CONCENTRATION OF
DILUTE SULPHURIC ACID SOLUTIONS**

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This invention relates to a process for the concentration of dilute sulfuric acid solutions, particularly dilute solutions containing iron (II) sulfate and other metal salts obtained, for example, during the production of titanium dioxide by the "sulphate" process.

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In the "sulphate" process, the raw material (ilmenite or slag) is ground and dissolved in concentrated sulphuric acid to give a solution of titanium sulphate. This solution is hydrolysed to convert the titanium sulphate to titanium dioxide which is filtered off. The solution remaining after filtration contains 10-30% by weight sulphuric acid as well as large amounts of iron (II) sulfate and other metal salts. In the following description, this sulfuric acid is designated as "waste acid".

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In order to be able to reuse the sulfuric acid in the waste acid, and particularly to be able to recycle it to the titanium dioxide manufacturing process, it is necessary to reconcentrate the waste acid and to separate the metal salts therefrom to the greatest possible extent. In the various known processes, the waste acid is reconcentrated to a concentration of 60 to 70% by weight sulphuric acid, the precipitated metal salts are separated out, and the reconcentrated acid is then either directly reused or concentrated further.

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As storing the waste acid is impractical, any factor which affects the efficiency of the concentration process, particularly if it results in the process having to be halted, also has an effect on the rate of titanium dioxide production.

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EP-A-425000 discloses a process for concentrating dilute sulphuric acid using a multistage system, each stage consisting of a heat exchanger and a vacuum evaporator. The heating medium used is steam and to increase the economics

of the process, the steam generated by the evaporation step in the second stage is used as the heating medium in the first stage.

5 It is well known that one of the problems associated with such a process using heat exchangers is that as the concentration of the acid increases, there is an increasing tendency for the salts to come out of solution and be deposited on the
10 surface of the heat exchanger, resulting in the process having to be halted whilst such deposits are removed.

15 Although the major component of the metal salts present is ferrous sulphate, deposition of this material does not produce a particularly difficult problem as such deposits, being water soluble, are easily removed by washing.

20 A much greater problem is caused when calcium sulphate is present in the dilute acid as this material is insoluble in water and hence removal of deposits is expensive and time consuming. Moreover, calcium sulphate is a very efficient
25 heat insulator and deposition rapidly affects the efficiency of the process.

The problem of calcium sulphate deposition is worst at acid concentrations
30 between circa 34% and 39%. Below these concentrations the calcium sulphate stays in solution and above them a precipitated salt phase forms (comprising ferrous sulphate as well as calcium sulphate) so there is no precipitation on
35 surfaces directly from solution.

According to EP-A-425000, the concentration of the acid in the first stage should
40 be kept at 40% or less, i.e. it is suggesting that the system should be operated in a manner leading to maximum calcium sulphate deposition.

EP-A-425000 also suggests that it may be useful to heat the dilute acid prior to the
45 concentration process using waste heat.

5 In accordance with common chemical engineering terminology, "waste heat" refers to heat, usually in the form of steam or hot water, which has been used previously as a heating medium and which is consequently at a lower temperature than when originally generated and is to be distinguished from "live" heat, again usually in the form of steam or hot water, which has been generated at a temperature suitable for a particular purpose.

10 A suitable source of such heat is hot water resulting from condensation of the steam used in steam micronisers which are commonly used to mill the titanium dioxide to produce pigment grade material.

15 A more economic process than described in EP-A-425000 is to use the waste heat in a heat exchanger/evaporation system. In accordance with the disclosure of EP-A-425000, the logical position of such a system is as a pre concentrator.

20 According to one aspect of the invention, there is provided a process for the concentration of dilute sulphuric acid containing metal salts using a multistage heat exchanger vacuum evaporator system, comprising the steps of

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- 30 a) feeding part of the acid to the first stage of the multistage system operating at an acid concentration of less than 30%.
- 35 b) feeding the remainder of the dilute acid to a separate heat exchanger vacuum evaporator using waste heat as the heating medium and operating at an acid concentration of greater than 40%.
- 40 c) feeding the acid from steps (a) and (b) to the second stage of the multistage system operating at a concentration of greater than 50% and recycling steam generated in the evaporator as the heating medium for
- 45 the first stage, and

- d) feeding the acid from the second stage to such subsequent steps as are necessary to produce the required final acid concentration.

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According to a further aspect of the invention, the process comprises the steps of

- a) feeding the dilute acid to the first stage of the multistage system operating at an acid concentration of less than 30%
- b) feeding part of the acid from step (a) to a heat exchanger/vacuum evaporator system heated using waste heat and operating at an acid concentration greater than 40%.
- c) feeding the acid from step (b) with the remainder of the acid from step (a) to the second stage of the multistage system operating at an acid concentration greater than 50% and recycling steam generated in the evaporator as the heating medium for the first stage, and
- d) feeding the acid from the second stage to such subsequent steps as are necessary to produce the required final acid concentration.

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In this manner, circulation of acid through a heat exchanger/evaporation stage at a concentration at which there is maximum calcium sulphate deposition, is avoided.

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In addition, interposing the stage in which waste heat is used as the heating medium between stages 1 and 2 means that the heat exchange between the steam generated in stage 2 and the relatively cooler acid in stage 1 is more efficient.

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The invention will be more readily understood from the following description drawing and example.

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In the drawing;

Figure 1 is a schematic diagram of a multistage, indirectly heated, evaporation system using steam as the heating medium; and

Figure 2 is a plan showing alternative configurations of a two-line system.

Referring to Figure 1, the multistage system shown consists of 3 stages, each consisting of a heat exchanger (10, 20, 30), a vacuum evaporator (11, 21, 31) and a pump (12, 22, 32) for circulating the acid around the heat exchanger/evaporator loop. Stages 2 and 3 are heated by "live" steam through lines 23 and 33 whereas Stage 1 is heated by the vapour produced in the evaporator 21 through line 13. Vapour produced in the evaporators 11 and 31 is removed to a condenser (not shown) through lines 14 and 34.

Dilute acid is fed into Stage 1 via line 15, the volume ratio of the dilute acid feed to the acid circulating in the loop being circa 1:100. Lines 16, 26 and 36 feed the increasingly concentrated acid, under gravity, from Stage 1 to Stage 2, Stage 2 to Stage 3 and from Stage 3 to further processing steps, for example, maturation and filtration.

In addition to the multistage system, the overall apparatus includes a single stage heat exchanger/vacuum evaporator system similar to the individual stages shown in Figure 1 except that the heating medium is waste heat provided, for example, by condensation of steam from steam micronisers. To distinguish this system from the multistage system, it is hereinafter designated as "Stage A".

In Figure 2, Configuration 1 shows the arrangement as suggested by the teaching of EP-A-425000, Configuration 2 shows the arrangement in accordance with the first aspect of the invention and Configuration 3 shows the arrangement in accordance with the second aspect of the invention.

5 In accordance with Configuration 1, the dilute acid to be treated is fed solely to Stage A operating at a concentration of <30%, the output from Stage A being fed to Stage 1 operating at a concentration of between 30% and 40%, i.e. at an acid concentration at which calcium sulphate deposition is a maximum. Stages 2 and 3 operate at circa 46% and 52% respectively and the output from Stage 3 is passed for further treatment, e.g. maturation and filtration.

10 In Configuration 2, the dilute acid is fed in a volume ratio of circa 2:6:1 to Stage 1 operating at an acid concentration of circa 30% and to Stage A operating at circa 40% concentration. Stages 2 and 3 operate in the same manner as in Configuration 1.

20 As an alternative, in configuration 3, all the dilute acid is fed to Stage 1 operating at a concentration of less than 30%. The output of Stage 1 is fed partly to Stage A operating at a concentration of circa 42% and partly to Stage 2 where it is mixed with the output of Stage A. Stage 2 operates at a concentration of circa 50%.

25 Hence in Configurations 2 and 3, none of the apparatus is operating at an acid concentration where calcium sulphate deposition is a major problem.

30 With Configuration 1, fouling of Stage 1 occurs at a rate of 1.0mm/week necessitating shut down and cleaning every three weeks. With Configuration 2 the cleaning interval is extendable to 3-9 months due to a reducing in fouling to less than 0.1mm/week. In addition, the maximum feed rate may be increased by circa 10% with the potential, in the case of Configuration 3, of an increase of 30%. Finally, it was found that Configuration 3 gave a 20% steam saving compared to Configuration 1.

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CLAIMS

- 5 1. A process for the concentration of dilute sulphuric acid containing metal salts using a multistage heat exchanger vacuum evaporator system, comprising the steps of
- 10 a) feeding part of the acid to the first stage of the multistage system operating at an acid concentration of less than 30%.
- 15 b) feeding the remainder of the dilute acid to a separate heat exchanger vacuum evaporator using waste heat as the heating medium and operating at an acid concentration of greater than 40%.
- 20 c) feeding the acid from steps (a) and (b) to the second stage of the multistage system operating at a concentration of greater than 50% and recycling steam generated in the evaporator as the heating medium for
- 25 the first stage, and
- 30 d) feeding the acid from the second stage to such subsequent steps as are necessary to produce the required final acid concentration.
- 35 2. A process for the concentration of dilute sulphuric acid containing metal salts using a multistage heat exchanger vacuum evaporator system, comprising the steps of
- 40 a) feeding the dilute acid to the first stage of the multistage system operating at an acid concentration of less than 30%
- 45 b) feeding part of the acid from step (a) to a heat exchanger/vacuum evaporator system heated using waste heat and operating at an acid concentration greater than 40%.

- 5
- c) feeding the acid from step (b) with the remainder of the acid from step (a) to the second stage of the multistage system operating at an acid concentration greater than 50% and recycling steam generated in the evaporator as the heating medium for the first stage, and
- 10
- d) feeding the acid from the second stage to such subsequent steps as are necessary to produce the required final acid concentration.

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3. A process according to claim 1, in which the dilute acid is fed to the first stage of the multistage system and the separate heat exchange vacuum evaporator in a ratio of 15:1 to 3.5:1.

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Fig. 1.

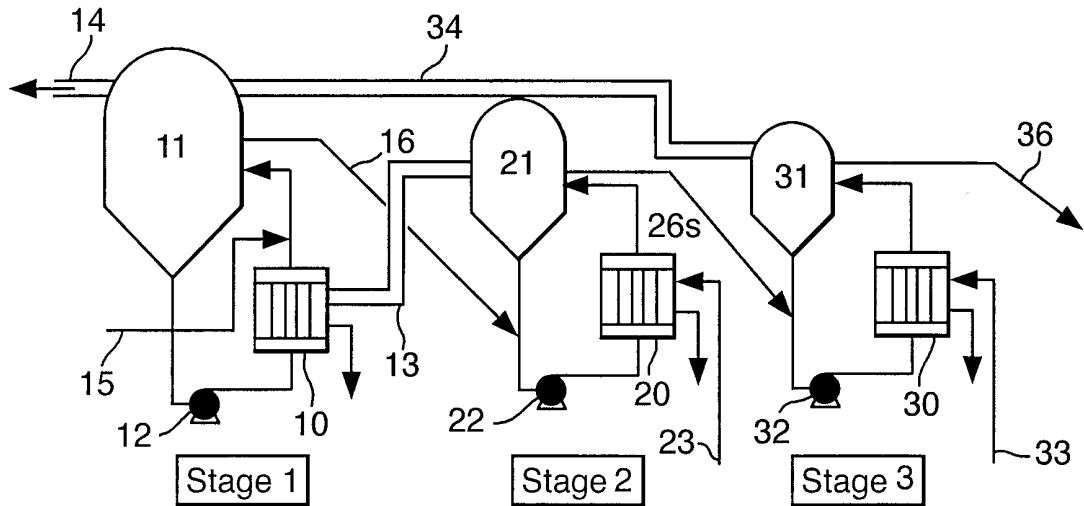
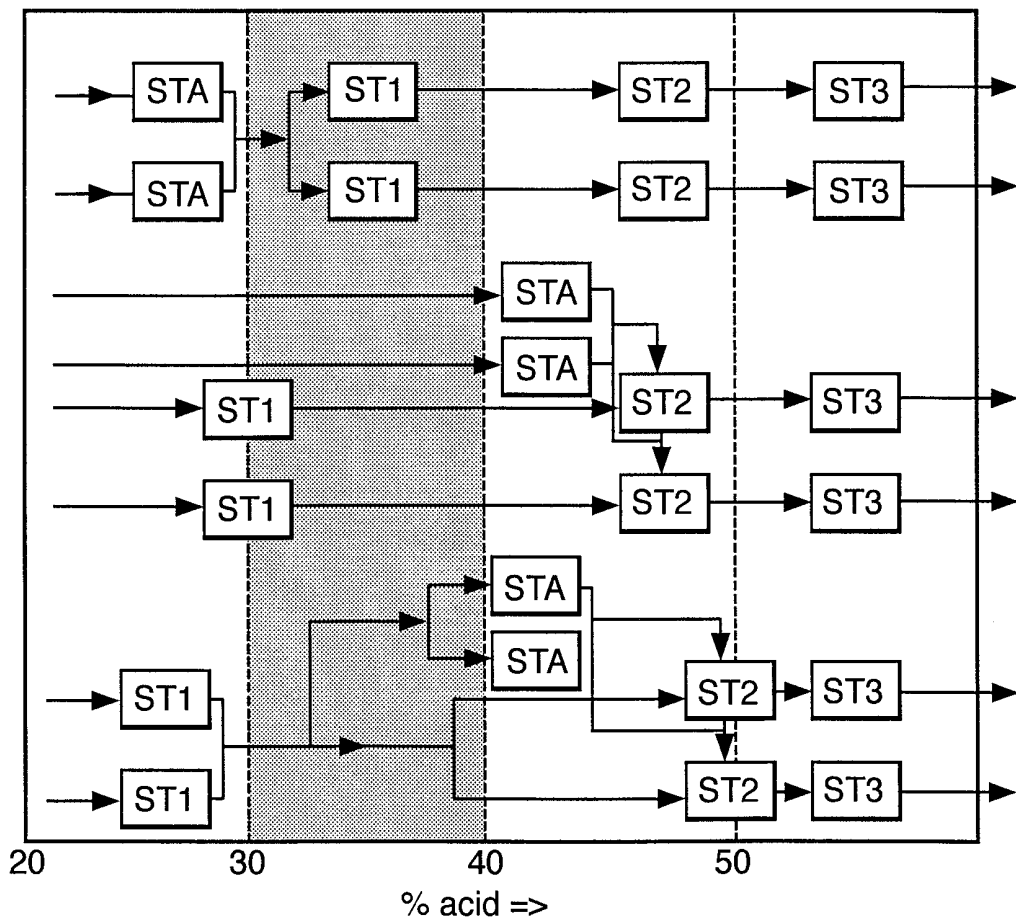


Fig. 2.



INTERNATIONAL SEARCH REPORT

International Application No

EP/GB 99/02486

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C01B17/88				
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) IPC 7 C01B				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
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C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
A	EP 0 429 933 A (BAYER AG) 5 June 1991 (1991-06-05) claim 1 ---	1		
A	EP 0 425 000 A (METALLGESELLSCHAFT AG) 2 May 1991 (1991-05-02) cited in the application claim 1 ---	1		
A	EP 0 476 744 A (METALLGESELLSCHAFT AG) 25 March 1992 (1992-03-25) claims 1-3 ---	1		
A	DE 26 18 122 A (KRONOS TITAN GMBH) 10 November 1977 (1977-11-10) claim 1 ---	1		
-/--				
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Date of the actual completion of the international search	Date of mailing of the international search report			
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International Application No

Fuji/GB 99/02486

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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Information on patent family members

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