595662

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 29-1-90

COMMONWEALTH OF AUSTRALIA

Patents Act 1952

NON- CONVENTION APPLICATION FOR A STANDARD PATENT

~~I~~/WE, YOSHIDA KOGYO K.K., a Japanese company of No. 1, Kanda Izumi-cho, Chiyoda-ku, Tokyo, Japan

hereby apply for the grant of a Standard Patent for an invention entitled:

METHOD AND APPARATUS FOR CONTINUOUS SYNTHESIS OF AQUEOUS ALUMINIUM SULFATE SOLUTION FROM ALUMINUM HYDROXIDE SLUDGE

which is described in the accompanying complete specification.

~~This application is made under the provision of Part XVl of the Patents Act 1952 and is based on an application for a patent or similar protection made~~

~~in~~ ~~on~~
~~No.~~ (

~~in~~ ~~on~~
~~No.~~ (

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LODGED AT SUB-OFFICE
16 NOV 1987
Sydney

Dated this 13th day of November 1987
YOSHIDA KOGYO K.K.

By: ____________________
Registered Patent Attorney

To: The Commissioner of Patents
COMMONWEALTH OF AUSTRALIA

FP 87-46-AU/YKK

Commonwealth of Australia
The Patents Act 1952
DECLARATION IN SUPPORT

In support of the (XXXXXXXXX) Application made by:

Yoshida Kogyo K. K. of No. 1, Kanda Izumicho, Chiyoda-ku, Tokyo 101, Japan

for a patent for an invention entitled: "METHOD AND APPARATUS FOR CONTINUOUS SYNTHESIS OF AQUEOUS ALUMINUM SULFATE SOLUTION FROM ALUMINUM HYDROXIDE SLUDGE"

I (~~We~~), Ichiro Agata, Director of Patent Department of Yoshida Kogyo K. K. of and care of the applicant company do solemnly and sincerely declare as follows:

---

a) XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

~~or~~

b) I am (~~We are~~) authorised by the applicant(~~s~~) for the patent to make this declaration on its behalf.

Delete the following if not a Convention Application.

~~The basic application(s) as defined by section 141 (142) of the Act was (were) made~~

~~in Japan~~ ~~on 16th May, 1987~~

~~in~~ ~~on~~

~~in~~ ~~on~~

~~by YOSHIDA KOGYO K.K.~~

~~The basic application(s) referred to in this paragraph is (are) the first application(s) made in a Convention country in respect of the invention the subject of the application.~~

---

a) ~~I am (We are) the actual inventor(s) of the invention~~

~~or~~

b) Hideo Yoshizaki, residing at 2945-15, Sumiyoshi, Uozu-shi, Toyama-ken, Japan

is (~~are~~) the actual inventor(~~s~~) of the invention and the facts upon which the applicant company is (~~are~~) entitled to make the application are as follows:

Applicant is Assignee of the above inventor, in respect of this invention.

Declared at Tokyo, Japan this 30th day of October 1987

Signed [signature] Status Director of Patent Department

Declarant's Name Ichiro Agata

F. B. RICE & CO PATENT ATTORNEYS

This form is suitable for any type of Patent Application. No legalisation required.

(12) PATENT ABRIDGMENT (11) Document No. AU-B-81232/87
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 595662

(54) Title
METHOD AND APPARATUS FOR CONTINUOUS SYNTHESIS OF AQUEOUS ALUMINUM SULFATE SOLUTION FROM ALUMINUM HYDROXIDE SLUDGE

International Patent Classification(s)
(51)[4] **C01F 007/74**

(21) Application No. : **81232/87** (22) Application Date : **16.11.87**

(43) Publication Date : **01.06.89**

(44) Publication Date of Accepted Application : **05.04.90**

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(57) Claim

1. A method for continuous production of an aqueous aluminum sulfate solution from by-products occurring in the work of aluminum surface treatment, which method is characterised by the steps of feeding aluminum sludge arising in said work of aluminum surface treatment and consisting mainly of aluminum hydroxide, waste sulfuric acid arising during the removal of coating in said work of surface treatment, and an aluminum sulfate-containing aqueous sulfuric acid solution arising during the recovery of sulfuric acid in said work of surface treatment to a reaction tank consisting of a plurality of component tanks, causing said fed substances to flow sequentially through a first tank through to a last tank to undergo reactions under temperature conditions in the range of 80°C to the boiling point of the reaction solution and, at the same time, feeding part of said aluminum sulfate-containing aqueous sulfuric acid solution to at least one of the tanks from the second tank through to the last tank, and adjusting the pH value of the reaction solution in the last tank at a level in a prescribed range of 1.6 to 2.5.

9. An apparatus for continuous production of an aqueous aluminum sulfate solution from by-products occurring in the work

of aluminum surface treatment, which apparatus is characterized by comprising:

a reaction tank consisting of first through n'th component tanks ~~adapted to permit~~ permitting continuous reactions respectively of aluminum sludge arising in the work of aluminum surface treatment and consisting mainly of aluminum hydroxide, waste sulfuric acid arising during the removal of coat in said work of surface treatment, and an aluminum sulfate-containing aqueous sulfuric acid solution arising during the recovery of sulfuric acid in said work of surface treatment,

a first feed pipe ~~for~~ feeding said aluminum sulfate-containing aqueous sulfuric acid solution to the ~~said~~ first tank,

an n'th feed pipe (n for an integer of the value of at least 2) ~~for~~ feeding said aluminum sulfate-containing aqueous sulfuric acid solution to at least one of the second and subsequent tanks,

a first pH indicator-controller-recorder disposed inside said first or second tank,

a first control valve interlocked with said first pH indicator-controller-recorder and controlling ~~adapted to control~~ the flow volume within said first feed pipe,

an n'th indicator-controller-recorder (n for an integer of the value of at least 2) disposed in at least one of said second and subsequent tanks, and

an n'th control valve (n for an integer having the value of at least 2) interlocked with said n'th indicator-controller-recorder and controlling ~~adapted to control~~ the flow volume within said n'th feed pipe.

COMMONWEALTH OF AUSTRALIA 595662

Patents Act 1952

COMPLETE SPECIFICATION

(ORIGINAL)

Application Number :
Lodged :

Complete Specification Lodged :
Accepted :
Published :

Priority :

Related Art :

This document contains the amendments made under Section 49 and is correct for printing.

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Complete Specification for the invention entitled:
METHOD AND APPARATUS FOR CONTINUOUS SYNTHESIS OF AQUEOUS ALUMINUM SULFATE SOLUTION FROM ALUMINUM HYDROXIDE SLUDGE
The following statement is a full description of this invention including the best method of performing it known to us:-

BACKGROUND OF THE INVENTION

1. Field of the Invention:

This invention relates to a method for continuous synthesis of an aqueous aluminum sulfate solution from the aluminum sludge separating, in a state containing aluminum hydroxide as a main component thereof, from the effluent originating in the step of treatment of alunminum for the production of Alumite (a product of aluminum having a corrosionproof coating formed thereon by anodization) operated by an aluminum-related enterprise and to an apparatus for effecting the method.

2. Description of the Prior Art:

In the work of Alumite treatment, as a pretreatment therefor, an aluminum blank is etched with a caustic soda solution to remove scratches or other similar flaws inflicted on the surface thereof and smoothen the surface. Otherwise in the work of reprocessing (recoating) a rejectable aluminum product, this product is treated with a caustic soda solution for the removal of an oxide coat therefrom. Further, the aluminum black is subejcted to a treatment for anodic oxidation and a treatment for electrolytic coloration in a sulfuric acid solution. During these treatments, Al ions are dissolved out of the aluminum blankinto the aforementioned solution and entrained thereby into an adjoining washing tank. The spent washing water is forwarded to the step for disposal of waste water. While the waste water is undergoing a neutralizing treatment, there occurs a white precipitate of aluminum hydroxide.

The waste liquid (slurry) consequently produced is generally caused by addition of an acrylamide type macromolecular flocculant to form a floc of high solidity. This floc is dehydrated to form an aluminum sludge (hereinafter referred to simply as "sludge") and the sludge is subjected to the subsequent treatment (to be discarded or recovered). This sludge is generally composed of 83 to 87% of water, 8 to 12% of $Al(OH)_3$, and 6 to 3% of impurities (such as SiO_2 and organic substances).

In the surface treatment of aluminum,an aqueous sulfuric acid solution is used for the removal of the coat from aluminum surface and the coat adhering to the surface of a jig. These works for the removal of coats give rise to waste sulfuric acid as a waste of aging. This waste sulfuric acid is generally composed of 75 to 90% of free H_2O and 2 to 0.5% of $Al_2SO_4)_3$.

From the standpoint of prevention of environmental pollution and preservation of resources, the sludge and the waste sulfuric acid rising from the works of aluminum surface treatment are generally utilized for the synthesis of aqueous aluminum sulfate solution. The reaction involved in the synthesis of aluminum sulfate, however, proceeds so quickly as to render control of reaction velocity difficult. Further, since the aluminum sulfate as a final product has the pH value thereof regulated to suit the purpose for which the product is put to use, the final pH value of the liquid for the synthesis must be adjusted so as to equal the pH value of the aluminum sulfate. Since this adjustment of the pH value is difficult, it has been held difficult to produce the aqueous aluminum sulfate solution by the method of continuous synthesis.

The synthesis of the aqueous aluminum sulfate solution from the sludge has been heretofore carried out exclusively by the so-called batchwise process, which generally comprises charging a vessel for the synthesis with a fixed amount of waste sulfuric acid and heating the contents of the vessel with a fixed amount of the sludge supplied gradually thereto.

The aforementioned conventional methodrequires the vessel for synthesis to be made of a material excellent in corrosion-proofness because the contents of the vessel are composed mainly of highly concentrated waste sulfuric acid during the initial stage of the synthesis. For example, vessels of the type provided with a glass lining are now in popular use for the synthesis. The vessel of this material has the disadvantage that it is expensive, entails difficult maintenance works of repair and inspection, and tends to break easily. Moreover, since the synthesis is made batchwise, the vessel used therefor is inevitably large and the driving power is proportionately large and the equipment as a whole is voluminous and occupies a large floor area. Thus, the synthesis entails a high cost of equipment and the vessel used therefor cannot be easily expanded for increase of capacity. Further, owing to the batchwise production, the synthesis has the disadvantage that the operation to be involved is complicated in procedure and inferior in efficiency and the vessel for the synthesis which is heated by means of a jacket is destined to suffer from gradual loss of thermal efficiency due to the phenomenon of scaling and entail a high running cost.

As one of the various kinds of waste occurring in the works of aluminum surface treatment, a dilute aqueous sulfuric acid solution arising, in a state containing aluminum sulfate (hereinafter referred to briefly as "sulfuric alum"), during the recovery of sulfuric acid from the electrolyte constitutes itself a problematic by-product besides the aforementioned sludge and waste sulfuric acid. The aqueous sulfuric acid solution containing this sulfuric alum has not occurred to any appreciable extent to date and, therefore, has been sufficiently coped with by the treatment of waste water. In recent years, various methods for the treatment of electrolytes such as the method using ion-exchange resins for separation and the method using diffuse transmission membranes for separation have advanced. Owing to the advance of these methods, the aqueous sulfuric acid solution containing the sulfuric alum is rapidly gaining in volume. In the operation of the method using an ion-exchange resin for separation, for example, part of the sulfuric acid-containing electrolyte in the electrolytic cell for the treatment of anodic oxidation or the treatment of AC coloration is subjected to an ion-exchange treatment. While the sulfuric acid recovered by this ion-exchange treatment is returned to the electrolytic cell, this treatment gives rise to a treated water containing part of the sulfuric acid and sulfuric alum. Also in the operation of the method using a diffuse transmission membrane, part of the electrolyte in the electrolytic cell is treated with the diffuse transmission membrane. While the sulfuric acid recovered by this treatment is returned to the electrolytic cell, the treatment produces a treated water containing part of the sulfuric acid and sulfuric alum. The dilute aqueous sulfuric acid solution containing the sulfuric alum generally contains 3 to 6% of H_2SO_4 and 7 to 9% of $Al_2(SO_4)_3$. In recent years, as the installation of facilities for the treatment of electrolytes has increased in ratio to keep place with the imporovement of quality of the aluminum surface treatment, this dilute aqueoussulfuric acid solution has been growing in volume. In the circumstances, the question as to how the dilute aqueous sulfuric acid solution ought to be safely disposed of has been driving the industry concerned to its wit's end. An idea may possibly be conceived of utilizing this solution for the aforementioned batchwise synthesis of an aqueous aluminum sulfate solution. The present applicant for patent himself is partially utilizing the solution for the synthesis. Since the aforementioned sulfuric alum-containing aqueous sulfuric acid solution is a dilute liquid, the use of this solution in an increased volume inevitably results in a decrease in the reaction velocity. Further, since the synthesis is made batchwise, it does not suit commercialization.

SUMMARY OF THE INVENTION

This invention, therefore, has been produced for the purpose of overcoming the drawbacks suffered by the prior art as described above. An object of the invention is to provide a method for permitting continuous synthesis of an aqueous aluminum sulfate solution by effective use of the sludge, waste sulfuric acid, and sulfuric alum-containing aqueous aluminum sulfate solution arising in the works of aluminum surface treatment and causing serious anxiety to the industry concerned regarding safe disposal thereof and an apparatus to be used for effecting the method.

Another object of this invention is to provide a method for continuous synthesis of an aqueous aluminum sulfate solution, which method excels in productivity, workability, safety, etc., operates with relatively inexpensive equipment, and affords the product in a high yield, and an apparatus for effecting the method.

Yet another object of this invention is to provide a method for effecting continuous synthesis of an aqueous aluminum sulfate solution with high energy efficiency at a low running cost and an apparatus for working the method.

To accomplish the objects described above according to the present invention, there is provided a method for continuous production of an aqueous aluminum sulfate solution from by-products occurring in the work of aluminum surface treatment, which method is characterized by the steps of feeding aluminum sludge arising in the work of aluminum surface treatment and consisting mainly of aluminum hydroxide, waste sulfuric acid arising during the removal of coating in the aforementioned work of surface treatment, and an aluminum sulfate-containing aqueous sulfuric acid solution arising during the recovery of sulfuric acid in the aforementioned work of surface treatment to a reaction tank consisting of a plurality of component tanks, i.e. first through n'th tanks, causing the fed substances to flow sequentially through the first tank through to the n'th tank (last tank) to undergo reactions under temperature conditions in the range of 80°C to the boiling point of the reaction solution and, at the same time, feeding part of the aforementioned aluminum sulfate-containing aqueous sulfuric acid solution to at least one of the tanks from the second tank through the last tank, and adjusting the pH value of the reaction solution in the ~~leat~~ last tank at a level in the range of 1.6 to 2.5.

In the method described above, the adjustment of the pH value of the reaction solution constitutes itself one of the important factors for efficient continuous synthesis aimed at. In accordance with the present invention, therefore, there is provided an apparatus for continuous production of the aqueous aluminum sulfate solution, which apparatus is designed in order for the adjustment of the pH value to be effected properly. This apparatus is characterized by comprising:

a reaction tank consisting of first through n'th components tanks ~~adapted to permit~~ permitting continuous reactions respectively of aluminum sludge arising in the work of aluminum surface treatment and consisting mainly of aluminum hydroxide, waste sulfuric acid arising during the removal of coat in the aforementioned work of surface treatment, and an aluminum sulfate-containing aqueous sulfuric acid solution arising during the recovery of sulfuric acid in the aforementioned work of surface treatment,

a first feed pipe ~~for~~ feeding the aforementioned aluminum sulfate-containing aqueous sulfuric acid solution to the ~~aforementioned~~ first tank, an n'th feed pipe (n for an integer of the value of at least 2) ~~for~~ feeding the aforementioned aluminum sulfate-containing aqueous sulfuric acid solution to at least one of the second and subsequent tanks,

a first pH indicator-controller-recorder disposed inside the aforementioned first or second tank,

a first control value interlocked with the aforementioned first pH indicator-controller-recorder and controlling ~~adapted to control~~ the flow volume within the aforementioned first feed pipe,

an n'th indicator-controller-recorder (n for an integer of the value of at least 2) disposed in at least one of the aforementioned second and subsequent tanks, and

an n'th control valve (n for an integer having the value of at least 2) interlocked with the aforementioned n'th indicator-controller-recorder and controlling ~~adapted to control~~ the flow volume within the aforementioned n'th feed pipe.

Further in the aforementioned method, the control of the temperture of the reaction solution also constitutes itself another important factor efficient continuous synthesis aimed at. In accordance with the present invention, therefore, there is provided an apparatus for reaction temperature control designed to permit continuous production of the aqueous aluminum sulfate solution from by-products occurring in the work of aluminum surface treatment, which apparatus is characterized by comprising:

the aforementioned reaction tank consisting of first through n'th component tanks, a first heat exchanger ~~for~~ effecting exchange of heat between the final aqueous aluminum sulfate solution emanating from the aforementioned reaction tank and possessing a boiling point approximating the boiling point of the reaction solution and the aforementioned aluminum sulfate-containing aqueous sulfuric acid solution,

a first, steam pipe disposed inside the aforementioned first tank,

a first temperature indicator-controller-recorder disposed inside the ~~aforementioned~~ first tank,

a first temperature control valve interlocked with the aforementioned first temperature indicator-controller-recorder and controlling ~~adapted to control~~ the flow volume of steam within the aforementioned first steam pipe,

an n'th steam pipe (n for an integer of the value of at least 2) and an n'th temperature indicator-recorder (n for an integer of the value of at least 2) disposed inside at least one of the aforementioned second and subsequent tanks, and

an n'th temperature control valve (n for an integer of the value of at least 2) interlocked with the aforementioned n'th temperature indicator-recorder and controlling ~~adapted to control~~ manually or automatically the flow volume of steam within the aforementioned n'th temperature indicator-recorder.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a flow sheet schematically illustrating a typical apparatus adapted to continuous synthesis of an aqueous aluminum sulfate solution according with the present invention.

Fig. 2 is a partial flow sheet schematically illustrating another embodiment of this invention, and

Fig. 3 is a partial longitudinal cross section another reaction tank usable in the apparatus according with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In the present invention, an aqueous aluminum sulfate solution is continuously synthesized by causing aluminum sludge occurring in the work of aluminum surface treatment, waste sulfuric acid occurring during the removal of a coat in the aforementioned work of surface treatment, and an aluminum sulfate-containing aqueous sulfuric acid solution occurring during the recovery of sulfuric acid in the aforementioned work of surface treatment to be reacted sequentially in a plurality of reaction tanks. The synthetic aluminum sulfate solution obtained at the end of these reactions is subjected to filtration and concentration to give rise to aluminum sulfate as a finished product. The attributes of the finished product depend on the final pH value of the synthetic aluminum sulfate solution and are regulated in a fixed range suitable for a particular purpose for which the finished product is used. In the present invention, the sulfuric alum-containing dilute aqueous sulfiric acid solution is utilized for the adjustment of the pH value of the reaction solution.

The reaction for the synthesis of aluminum sulfate is represented by the following formula (1) and the reaction formula for the sake of calculation is represented by the following formula (2).

$$2Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H_2O \qquad (1)$$

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O \qquad (2)$$

The reaction velocity constant in the reaction mentioned above and the effect of pH on the reaction were studied using a sludge, a waste sulfuric acid, and a sulfuric alum-containing dilute aqueous sulfuric acid solution possessing respective compositions indicated in Table 1 below.

Table 1

Composition	Sludge	Waste sulfuric acid	Sulfuric alum-containing aqueous sulfuric acid solution
$Al(OH)_3$	9.5%	-	
H_2O	86.8%	) 9.4%	) 85.8§
Other substances (such as micro-molecular flocculant)	3.7%		
H_2SO_4	-	90.0%	5.3%
$Al_2(SO_4)_3$		0.6%	8.7%

Since the reaction of the aforementioned three materials was experimentally demonstrated to be regarded as a homogenous second order reaction, thevelocity constant of the reaction was determine by a batch rest. From the results of the test, it is found that the velocity constant at 90° to 100°C was 0.12 ~ 0.671 ℓ/Al_2O_3·mol·sec. The results of various runs of the test conducted using the three materials in varied mixing ratios indicate that the proper value of the velocity constant ought to exceed at least 0.01 $\ell/Al_2O_3\cdot mol\cdot sec$. In view of commercial operation of the synthesis, the highest permissible limit of the velocity constant is 2.0 $\ell/Al_2O_3\cdot mol\cdot sec$.

If the pH value is unduly high, namely the amount of free H_2SO_4 is undully small, the reaction velocity is too low for the synthesis to be commercially feasible. In consideration of the fact that the final pH value of the synthetic solution is subject to control, therefore, it is most desirable in the case of continuous reaction to control this continuous reaction in such a manner that the pH value of the reaction solution in the first tank in the compound of reaction tanks will be lowered to heighten the reaction velocity and the pH values of the reaction solutions in the subsequent tanks will be gradually increased sequentially to adjust the final pH value of the synthetic solution eventually to the prescribed level. As the result of an experiment conducted by the inventors, it has been found that when the sludge, the waste sulfuric acid, and the sulfuric alum-containing dilute aqueous sulfuric acid solution are continuously fed in a fixed gravimetric ratio to a multi-stage (3 to 6 stages) reaction tank having the component stages provided with respectively fixed volumes commensurate with the intended volumes of treatment at respecitvely fixed temperatures (in the range of 80°C to the boiling point of the reaction solution, preferably 90°C to the boiling point), the synthetic aluminum sulfate solution possessing a pH value (in the range of 1.6 to 2.5, preferably 1.8 to 2.0) resulting from completion of the reaction is continuously obtained from the final stage of the reaction tank. The sulfuric alum-containing dilute sulfuric acid solution is fed in such a manner that the pH values of the reaction solutions in the component tanks will be retained at respectively prescribed levels. For the purpose of increasing the reaction velocity thereby producing the aqueous aluminum sulfate solution in an increased yield, it is desirable to control the pH value in the first reaction tank in the range of 0.1 to 1.0. For commercial operation of the synthesis, it suffices to control this pH value in the range of 0.1 to 2.0.

Now, the present invention will be described in detail below with reference to working examples of the present invention depicted in the accompanying drawings.

Fig. 1 is a flow sheet schematically illustrating a typical apparatus adapted to effect continuous synthesis of an aqueous aluminum sulfate solution by the multi-stage tank type parallel-flow reaction of the present invention. In the diagram, 1 stands for a belt conveyor for forwarding sludge having aluminum hydroxide as a main component thereof, 2 for a mixing tank, 3 for a reaction tank consisting of first through n'th tanks, 4 for a tank for holding a sulfuric alum-containing dilute aqueous sulfuric acid solution, and 5 for a waste sulfuric acid tank.

The reaction tank illustrated in Fig. 1 represents a case satisfying n = 5, i.e. using five ~~fine~~ component tanks. The first tank R_1 and the second tank R_2 are partitioned with a weir-like bulkhead 8a raised upright so as to permit overflow. The second tank R_2 and the third tank R_3, the third tank R_3 and the fourth tank R_4, and the fourth tank R_4 and the fifth tank R_5 are severally partitioned with respective bulkheads 8b suspended from above so as to form openings in the bottom parts thereof. These component tanks are each provided with a stirrer 9 adapted to be rotated by an electric motor M.

The sludge is fed as carried on the belt conveyer ~~coneyor~~ 1 to the mixing tank 2. In the meantime, the sulfuric alum-containing dilute aqueous sulfuric acid solution kept at normal room temperature in the dilute sulfuric acid solution tank 4 is forwarded by a pump 10 via a feed line 11 to a first heat exchanger 6, wherein the solution is heated to a temperature of about 65° to 70°C through exchange of heat with the produced synthetic aluminum sulfate solution possessing a temperature of about 100°C, and then forwarded to a second heat exchanger 7, wherein the solution is heated to a still higher temperature of about 95° to 100°C through exchagne of heat with steam possessing a temperature of boiling point, and thereafter fed to the mixing tank 2 through a first feed pipe 12. Part of the heated solution is fed to the fourth tank R_4 preceding the last tank through a second feed pipe 13. The mixture formed of the sludge with the sulfuric alum-containing aqueous sulfuric acid solution inside the mixing tank 2 is now in a state kept at an elevated temperature of about 70° to 80°C, mixed with the stirrer 9, and then forwarded to the first reaction tank R_1. Meanwhile, the waste sulfuric acid held inside the waste sulfuric acid tank 5 is forwarded by a pump 14 to a waste sulfuric acid receiving tank 15, deprived of floating substances with a screen 16 disposed inside the receiving tank 15, and then forwarded to the first reaction tank R_1 by a pump 17.

In the reaction tank 3, the reaction solution formed inside the first tank R_1 of the mixture of sludge, waste sulfuric acid, and sulfuric alum-containing aqueous sulfuric acid solution is caused to flow from the first tank R_1 to the final fifth tank R_5 as kept stirred by the stirrer 9 and undergo reactions represented by the formula (1) mentioned above. As the result, the synthetic aluminum sulfate solution is obtained at about 100°C from the fifth tank R_5. This solution is forwarded by a pump 18 through a produced solution line 19 and the first heat exchanger 6 to a filtration-purification unit (not shown).

Now, the control system will be described below. First, as regards the control of the pH value of the reaction solution, the pH value of the reaction solution in the first tank R_1 and the second tank R_2 is fixed at a level of about 0.8. When the actual feed amount of the sludge is changed so as to fall far below the theoretical feed amount, the feed amount of the waste sulfuric acid is proportionately increased, with the result that the pH value shifts from the fixed level, pH 0.8, toward the acidic side (to pH 0.2, for example). In this case, therefore, the pH value must be controlled. This adjustment of the pH value is effected by a first pH indicator-controller-recorder (PHICR) 20 which is disposed inside the second tank R_2. When the reading of pH value on the first pH indicator-controller-recorder is below 0.8 (strongly acidic side), a first control valve 21 disposed in the first feed pipe 12 for the sulfuric alum-containing dilute aqueous sulfuric acid solution and interlocked with the aforementioned recorder 20 is closed. Conversely when the reading of pH value is above 0.8, the first control valve 21 is opened. Thus, the pH value of the initial reaction solution is automatically controlled to 0.8 by suitable control of the feed amount of the sulfuric alum-containing dilute aqueous sulfuric acid solution.

The adjustment of the pH value in the first tank is normally effected as described above. If the actual feed amount of the sludge increases beyond the prescribed level as when the operation of the apparatus is resumed after a stop or when the pH value in the first tank is appreciably varied from the prescribed level by a certain other factor, it naturally follows that the pH value of the first tank R_1 deviates from the prescribed level. For the purpose of returning the pH value to within the fixed range, the waste sulfuric acid having a lower pH value (strongly acidic side) than the aforementioned sulfuric alum-containing dilute aqueous sulfuric acid solution may be used in the place of the dilute aqueous solution just mentioned. When the reading of pH value on the first pH indicator-controller-recorder 20 is below 0.8, the supply of the waste sulfuric acid is discontinued by turning off the pump 17 of the waste sulfuric acid receiving tank 15. When the reading of pH is above 0.8, the pump 17 is opened and the capacity thereof is increased (by opening the valve) to start feeding the waste sulfuric acid to the first tank R_1. Thus, the pH value is automatically controlled to 0.8. The suitable increase or decrease of the feed amount of the waste sulfuric acid possessing a low pH value is advantageous for pH adjustment particularly where the pH value heavily deviates because the time required for the pH value to return to within the fixed range is smaller than when the sulfuric alum-containing dilute aqueous sulfuric acid solution is used. It will be readily understood by persons skilled in the art that this pH adjustment can be accomplished by using both the sulfuric alum-containing dilute aqueous sulfuric acidsolution and the waste sulfuric acid.

Optionally, the first pH indicator-controller-recorder 20 may be disposed inside the first tank R_1 and adapted to detect the pH value on the outlet side of the first tank R_1. As the reaction proceeds, the pH value of the reaction solution increases and shifts toward the weakly acidic side. When the pH value of the synthetic aluminum sulfate solution within the fifth tank (last tank) R_5 falls on the strongly acidic side below the prescribed level (1.6 to 2.5, preferably 1.8 to 2.0), the detector of a second pH indicator-controller-recorder (RPHCR) 22 disposed inside the fifth tank R_5 detects this deviation of the pH value and closes a second control valve 23 disposed in the second feed pipe 13 for the sulfuric alum-containing dilute aqueous sulfuric acid solution. When the pH value conversely rises above the prescribed level, the aforementioned detector automatically opens the second control valve 23. It is permissible to connect feed pipes for the sulfuric alum-containing dilute aqueous sulfuric acid solution one each to the component tanks, disposing pH indicator-cntroller-recorders one each in the component tanks, and effect fine adjustment of the pH values of the reaction solution in the component tanks by the procedure described above. In any event, since the adjustment of the pH value of the reaction solution is effected by controlling the feed amount of the sulfuric alum-containing dilute aqueous sulfuric acid solution and/or that of the waste sulfuric acid and further since the pH value of the reaction solution is not less than 0.8 and the conversion in the first tank is about 90% and the pH value in the second tank cannot fall below the aforementioned level, it suffices to use stainless steel of the grade of about SUS 316 JIL as the material for the first tank and stainless steel of the grade of about SUS 316 L as the material forthe second and subsequent tanks.

Then, as regards the control of the temperature of the reaction solution, the temperature of the mixture of the sludge and the sulfuric alum-containing dilute aqueous sulfuric acid solution inside the mixing tank 2 is elevated to a level in the range of 70° to 80°C owing to the supply of the sulfuric alum-containing dilute aqueous sulfuric acid solution which possesses a temperature in the range of about 95° to 100°C. The sulfuric alum-containing dilute aqueous sulfuric acid solution kept at room temperature inside the dilute sulfuric acid tank 4 is heated, as described above, to a level of about 65° to 70°C (as detected by a temperature indicator-recorder (TR) 24) by means of the first heat exchanger and then elevated further to a level of about 95° to 100°C by means of the second heat exchanger 7. This temperature is detected by a temperature indicator-controller-recorder (TRC) 25 disposed behind the second heat exchanger 7 in the feed line for the sulfuric alum-containing dilute sulfuric acid solution. When the temperature so detected is below the prescribed level, a steam control valve 27 disposed in a steam feed pipe 26and interlocked with the aforementioned recorder 25 is opened.

When the detected temperature is above the prescribed level, the steam control valve 27 is narrowed. By thus controling the amount of steam entering the second heat exchanger 7, the temperature is automatically controlled to the prescribed level. To the reaction tanks are connected steam feed pipes. A first steam pipe 28 is immersed in the form of a coil or a planar plate in the reaction solution held inside the first tank R_1 and then ˙ed to a waste discharge groove 32 so as to effect exchange of heat. To the second through fourth tanks, a second steam pipe 29, a third steam pipe 30, and a fourth steam pipe 31 are respectively connected so as to effect introduction of steam. The temperature of the reaction solution inside the first tank R_1 is controlled by a first temperature indicator-controller-recorder (TRC) 33 and a first temperature control valve 34 disposed in the aforementioned first steam pipe 28 and interlocked with the aforementioned recorder 33. When the temperature of the reaction solution in the first tank R_1 is above the prescribed level, the first temperature control valve 34 is narrowed. When this temperature is below the prescribed level, the control valve 34 is opened. Thus, the temperature is automatically controlled to the prescribed level. To the third and fifth tanks R_3 and R_5 are respectively connected a third and a fifth temperature indicator-recorder (TR) 35 and 36. Depending on the temperatures detected by these temperature indicator-recorders 35 and 36, the control of temperature is manually effected by opening or closing second through fourth control valves 37 through 39. Optionally, the temperature of the reaction solution may be automatically effected by disposing temperature indicator-controller-recorders one each in the component tanks and interlocking these recorders to the respective temperature control valves in the steam pipes. Where the system is designed so as to elevate the temperature by introducing steam into the component tanks, the reaction solution is diluted and consequently suffered to entail use of extra energy in the subsequent work of purification. It is, therefore, desirable to effect the elevation of the temperature of the reaction solution in the first tank by the exchange of heat between the steam pipe and the reaction solution as illsutrated in the diagram.

Further in Fig. 1, the reference numeral 40 stands for a liquid level indicator-controller (LC) in the waste sulfuric acid receiving tank 15 for preventing the motor of the pump 17 from idle rotation. It automatically actuates the pump 14 when the liquid level of waste sulfuric acid in the waste sulfuric acid receiving tank 15 falls below a fixed line mark and it stops the operation of the pump when the liquid level rises above the mark. The reference numeral 41 stands for a liquid level indicator-controller (LICA) provided with an alarm and adapted to control the liquid level of the reaction tank 3. It automatically narrows a control valve 42 when the liquid level of the reaction solution falls below the fixed mark and it opens the control valve 42 when the liquid level rises above the mark. The reference numeral 43 stands for a cumulative flow amount indicator (FIQ) adapted to display the feed amount of the sulfur alum-containing dilute aqueous sulfuric acid solution. Continuous synthesis of an aqueous aluminum sulfate solution was carried out with the apparatus of Fig. 1 under the following conditions.

Conditions of synthesis

Sludge:

Feed amount	-	1,429 kg/hour	
Composition	-	$Al(OH)_3$	9.5% by weight
		Impurities	3.7% by weight
		H_2O	86.8% by weight

Waste sulfuric acid:

Feed amount	-	72.6 liters/hour	
Composition	-	Free H_2SO_4	90.0% by weight
		$Al_2(SO_4)_3$	0.6% by weight
Specific gravity	-	1.804 (25°C)	

Sulfuric alum-containing aqueous sulfuric acid solution

Feed amount	-	3,112 liters/hour	
Composition	-	Free H_2SO_4	5.3% by weight
		$Al_2(SO_4)_3$	8.9% by weight
		H_2O	Balance
Specific gravity	-	1.134 (12°C)	

Reaction temperature: 99° to 100°C

pH value of first tank: About 0.8

pH value of fifth tank: About 2.0

As the result, the aqueous aluminum sulfate solution could be continuously synthesized at a conversion of about 98%. The aqueous aluminum sulfate solution thus obtained was subjected to a filtration test under the conditions, i.e. 300 ml as the amount of synthetic solution used, 20°C as the filtration temperature, filtration under a vacuum (without filtration aid) as the manner of filtration, 95 cm² as the available area of filtration, Filter Paper, #2, of Toyo Roshi Co., Ltd., and 120 Torr as the filtration pressure (degree of vacuum). The test revealed no problem as to the filtration property of the solution.

Fig. 2 illustrates another typical apparatus for continuous synthesis of an aqueous aluminum sulfate solution of this invention, depicting the only portions with respect to which this apparatus differs from the apparatus of Fig. 1. The devices (such as, for example, waste sulfuric acid tank and heat exchangers), the measuring instruments (such as, for example, pH indicator-controller-recorders), and the feed lines (such as, for example, feed line for sulfuric alum-containing aqueous sulfuric acid solution) which are not shown in Fig. 2 are identical to those shown in Fig. 1. The apparatus illustrated in Fig. 1 is provided with the mixing tank 2. This mixing tank is disposed as illustrated simply because no reaction tank can be installed below the belt conveyor where the existing apparatus is adopted in its unmodified state. This installation of the mixing tank is not always necessary. As illustrated in Fig. 2, the aforementioned three raw materials can be directly fed to the first tank R_1 of the reaction tank 3 instead. In the apparatus of Fig. 2, the sludge is forwarded by a pump through a sludge feed pipe 44. Of course, it can be forwarded by a belt conveyor as in the apparatus of Fig. 1. In the reaction tank 3 illustrated in Fig. 2, the component tanks R_1 through R_5 are partitioned alternately with weir-like bulkheads 8a and bulkheads 8b suspended from above so as to prevent otherwise possible short pass of the reaction solution. For the purpose of more effectively preventing the short pass of the reaction solution, the component tanks may be provided therein with a baffle plate 53 as illustrated in Fig. 3.

The control of the temperature of the reaction solution in the first tank R_1 is automatically effected, similarly to the aforementioned apparatus of Fig. 1, by causing the first temperature indicator-controller-recorder 33 to control the first temperature control valve 34 disposed in the first steam pipe 28. By the same token, the temperatures of the reaction solution in the second through 4th tanks R_2 through R_4 are automatically controlled by means of second through fourth temperature indicator-controller-recorders (TRC) 45 through 47 disposed in the respective component tanks and second through fourth temperature control valves 48 through 50 disposed respectively in the second through fourth steam pipes 29 through 31. Further, the temperatures of the component tanks are controlled by exchange of heat between the portions of the reaction solution inside the component tanks and the second through fourth steam pipes immersed in the form of a coil or a planar sheet in the reaction solution.

The apparatus illustrated in Fig. 2 is provided with a synthetic solution circulation line 52 which issues from the discharge side of the pump 18 for discharge of the synthetic solution and returns into the first tank R_1. This circulation line 52 is provided therein a manual valve 51. Owing to this device, the aqueous aluminum sulfate solution can be returned to the first tank R_1 by opening the manual valve 51 when the second pH indicator-controller-recorder (PHICR) 22 (Fig. 1) serving to display the pH value of the synthetic solution displays an abnormal value (outside the prescribed range). Of course, the apparatus of Fig. 1 may be provided with the circulation line.

It is evident from the description given above, the following effects and advantages are derived from the present invention.

a) Since the synthesis of the aqueous aluminum sulfate solution is carried out continuously by the multi-stage tank type parallel reaction, the capacity for production is notably improved as compared with the conventional synthesis by the batchwise operation and, for a fixed volume of production, the apparatus permits a generous reduction in overall size and floor area. The apparatus, when necessary, may be installed indoors.

b) Since the adjustment of the pH values of the reaction system is effected by the use of the sulfuric alum-containing dilute aqueous sulfuric acid solution, the pH adjustment can be attained easily and the free H_2SO_4 concentration in the first tank is low. By controlling the pH values of the reaction solution in the component tanks in the range of 0.8 to 2.5, therefore, the reaction tanks made of stainless steel can be safely used. The reaction tanks, accordingly, can be given necessary maintenance by proper welding, repair, and inspection. Thus, the cost of equipment is low. Since the apparatus is continuously operated, the pH value of the reaction solution can be continuously controlled without requiring the valves, pumps, stirrers, etc. to be switched from time to time. The apparatus, therefore, can be easily automated. It is also effective in improving the workability and the safety.

c) On the basis of the experimental data on the reaction velocity constant, the capacity for production can be increased with a minor modification of the apparatus.

d) The system of the present invention for reaction temperature control entails virtually no loss of thermal efficiency due to scaling because the heating is effected by the use of the heat exchange units installed independently of the reaction tanks. Further, the control of the temperature can be effected automatically. Owing to the ease of temperature control coupled with the effect of continuous operation, the apparatus enjoys high energy efficiency and low power consumption and a low running cost as well.

The other advantages and effects of the present invention will be apparent from the foregoing description of the invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method for continuous production of an aqueous aluminum sulfate solution from by-products occurring in the work of aluminum surface treatment, which method is characterised by the steps of feeding aluminum sludge arising in said work of aluminum surface treatment and consisting mainly of aluminum hydroxide, waste sulfuric acid arising during the removal of coating in said work of surface treatment, and an aluminum sulfate-containing aqueous sulfuric acid solution arising during the recovery of sulfuric acid in said work of surface treatment to a reaction tank consisting of a plurality of component tanks, causing said fed substances to flow sequentially through a first tank through to a last tank to undergo reactions under temperature conditions in the range of 80°C to the boiling point of the reaction solution and, at the same time, feeding part of said aluminum sulfate-containing aqueous sulfuric acid solution to at least one of the tanks from the second tank through to the last tank, and adjusting the pH value of the reaction solution in the last tank at a level in a prescribed range of 1.6 to 2.5.

2. The method according to claim 1, wherein part of the aqueous aluminum sulfate solution emanating from the final tank is returned to the reaction tank when the pH value of the reaction solution in the final tank departs from the prescribed range.

3. The method according to claim 2, wherein part of the aqueous aluminum sulfate solution emanating from the final tank is returned to the first tank.

4. The method according to any of Claims 1 through 3, wherein the pH value of the reaction solution in the first or second tank is adjusted in the range of 0.1 to 2.0.

5. The method ~~accordign~~ according to Claim 4, wherein the adjustment of the pH value of the reaction solution is effected by controlling the amount of said aluminum sulfate-containing aqueous sulfuric acid solution fed to the first tank.

6. The method according to any of Claims 1 through 5, wherein the control of the temperature of the reaction solution in the reaction tank is carried out by feeding steam to said reaction solution.

7. The method according to any of Claims 1 through 5, wherein the control of the temperature of the reaction solution in the reaction tank is carried out by exchange of heat between said reaction solution and a steam pipe immersed in said reaction solution.

8. The method according to any of Claims 1 through 7, wherein said aluminum sulfate-containing aqueous sulfuric acid solution heated to an elevated temperature is fed to the first tank.

9. An apparatus for continuous production of an aqueous aluminum sulfate solution from by-products occurring in the work of aluminum surface treatment, which apparatus is characterized by comprising:

a reaction tank consisting of first through n'th component tanks ~~adapted to permit~~ permitting continuous reactions respectively of aluminum sludge arising in the work of aluminum surface treatment and consisting mainly of aluminum hydroxide, waste sulfuric acid arising during the removal of coat in said work of surface treatment, and an aluminum sulfate-containing aqueous sulfuric acid solution arising during the recovery of sulfuric acid in said work of surface treatment,

a first feed pipe ~~for~~ feeding said aluminum sulfate-containing aqueous sulfuric acid solution to the ~~said~~ first tank,

an n'th feed pipe (n for an integer of the value of at least 2) ~~for~~ feeding said aluminum sulfate-containing aqueous sulfuric acid solution to at least one of the second and subsequent tanks,

a first pH indicator-controller-recorder disposed inside said first or second tank,

a first control valve interlocked with said first pH indicator-controller-recorder and controlling ~~adapted to control~~ the flow volume within said first feed pipe,

an n'th indicator-controller-recorder (n for an integer of the value of at least 2) disposed in at least one of said second and subsequent tanks, and

an n'th control valve (n for an integer having the value of at least 2) interlocked with said n'th indicator-controller-recorder and controlling ~~adapted to control~~ the flow volume within said n'th feed pipe.

10. The apparatus according to Claim 9, wherein said n'th feed pipe serves to feed said aluminum sulfate-containing aqueous sulfuric acid solution to the tank immediately preceding the last tank, said n'th pH indicator-controller-recorder is disposed in the final tank, and said n'th control valve is disposed in said feed pipe.

11. The apparatus according to Claim 9 or Claim 10, wherein said reaction tank is divided into said first through n'th tanks by bulkheads suspended from above so as to form an opening on the bottom part of said reaction tank and/or weir-like bulkheads raised upright so as to allow overflow of the reaction solution.

12. The apparatus according to Claim 11,wherein a baffle plate adapted to prevent short pass of the reaction solution is disposed in at least one of said first through n'th tanks.

13. An apparatus for reaction temperature control to permit continuous production of an aqueous aluminum sulfate solution from by-products occurring in the work of aluminum surface treatment, which apparatus is characterized by comprising:

a reaction tank consisting of first through n'th component tanks ~~adapted to permit~~ permitting continuous reactions respectively of aluminum sludge arising in the work of aluminum surface treatment and consisting mainly of aluminum hydroxide, waste sulfuric acid arising during the removal of coat in said work of surface treatment, and an aluminum sulfate-containing aqueous sulfuric acid solution arising during the recovery of sulfuric acid in said work of surface treatment ~~treatemnt~~,

a first heat exchanger ~~for~~ effecting exchange of heat between the final aqueous aluminum sulfate solution emanating from said reaction tank and possessing a boiling point approximating the boiling point of the reaction solution and said aluminum sulfate-containing aqueous sulfuric acid solution, a first steam pipe disposed inside said first tank,

a first temperature indicator-controller-recorder disposed inside said first tank,

a first temperature control valve interlocked with said first temperature indicator-controller-recorder and ~~adapted to control~~ controlling the flow volume of steam within said first steam pipe,

an n'th steam pipe (n for an integer of the value of at least 2) and an n'th temperature indicator-recorder (n for an integer of the value of at least 2) disposed inside at least one of said second and subsequent tanks, and

an n'th temperature control valve (n for an integer of the value of at least 2) interlocked with said n'th temperature indicator-recorder and controlling adapted to control manually or automatically the flow volume of steam within said n'th temperature indicator-recorder.

14. A method for continuous production of an aqueous aluminum sulfate solution substantially as hereinbefore described with reference to the accompanying drawings.

15. An apparatus for continuous production of an aqueous aluminum sulfate solution substantially as hereinbefore described with reference to the accompanying drawings.

DATED this 24 day of January 1990

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Applicant:

F.B. RICE & CO.

FIG. 1

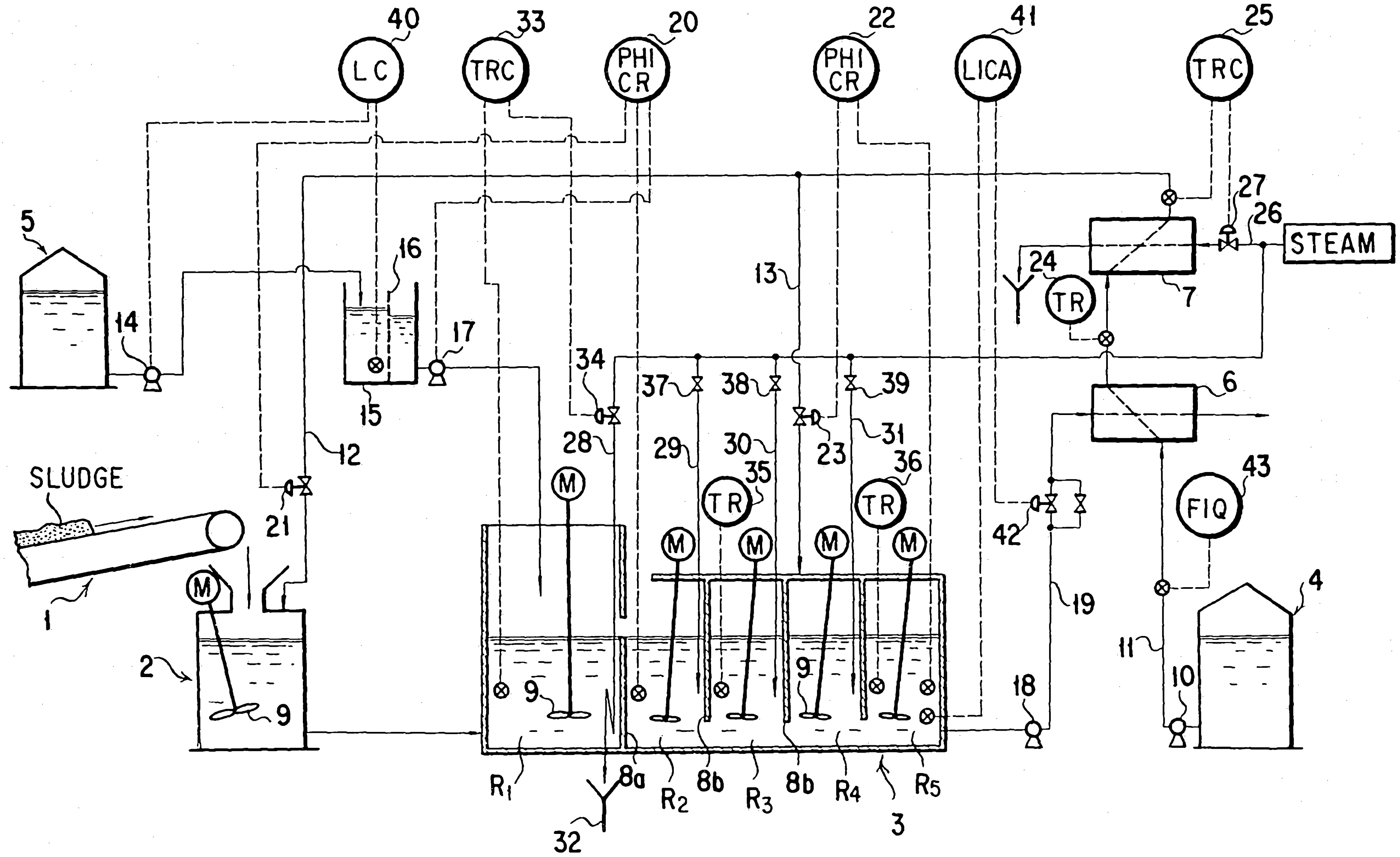
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FIG. 2

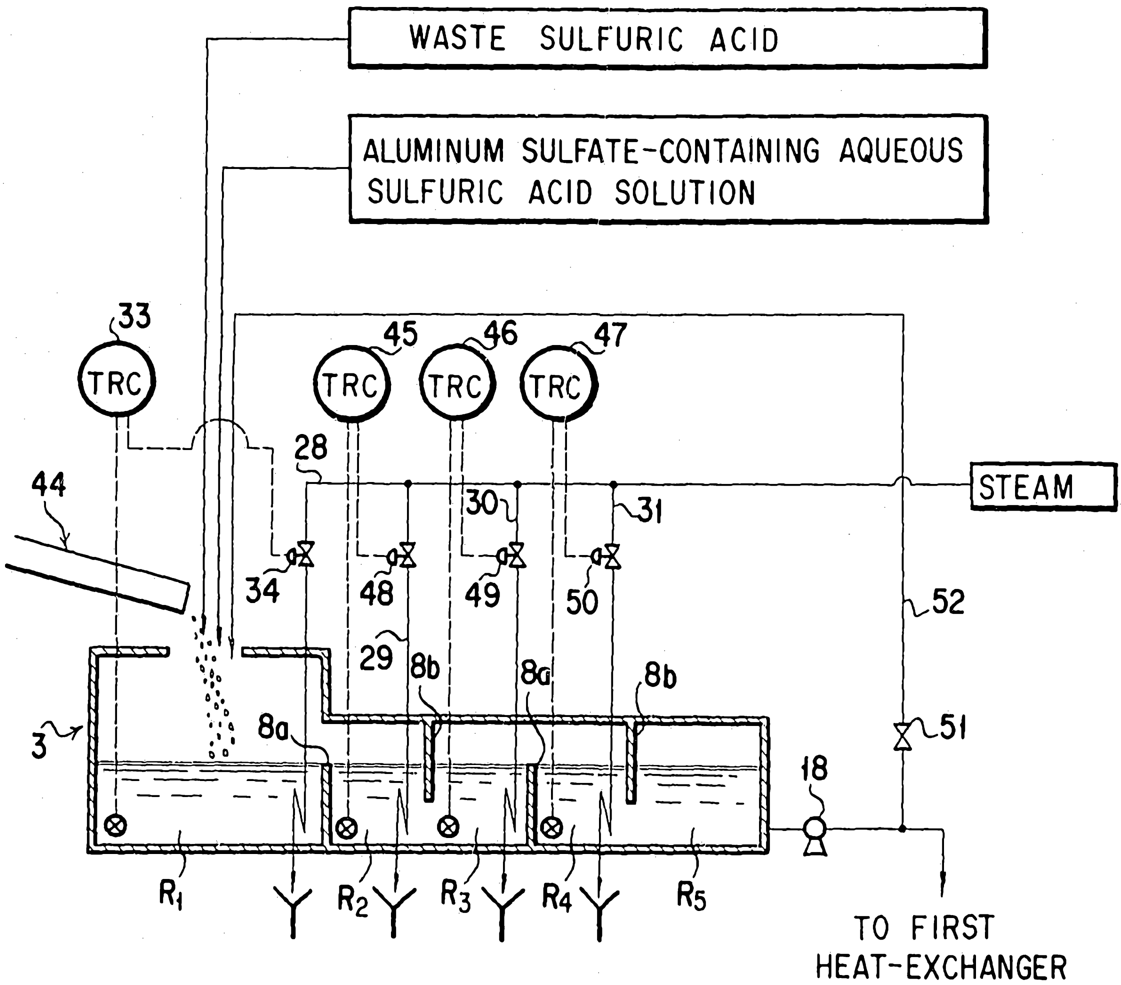

FIG. 3