

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

This invention relates to a method and apparatus for the continuous synthesis of an aqueous aluminum sulfate solution from an aluminum sludge, containing aluminum hydroxide as a main component, obtained as an effluent in the treatment of aluminum for the production of Alumite (an aluminum product having a corrosion proof coating formed thereon by anodization).

In the Alumite treatment process, as a pretreatment step, an aluminum blank is etched with a caustic soda solution to remove scratches or other similar flaws and to smooth its surface. Also, when reprocessing (recoating) a rejected aluminum product, this product is treated with a caustic soda solution to remove the oxide coat therefrom. Subsequently, the pretreated aluminum blank is subjected to anodic oxidation and to electrolytic coloration in a sulfuric acid solution. During these treatments, aluminum ions are dissolved out of the aluminum blank into the acid solution and entrained thereby into an adjoining washing tank. The spent washing water is forwarded to a step for the disposal of waste water. While the waste water is

undergoing a neutralizing treatment, a white precipitate of aluminum hydroxide is formed.

The waste liquid (slurry) consequently produced is generally flocculated by the addition of an acrylamide type macromolecular flocculant to form an aluminum sludge (hereinafter referred to simply as "sludge") and the sludge is subjected to subsequent treatment (to be discarded or recovered). The sludge generally comprises 83 to 87% of water, 8 to 12% of $\text{Al}(\text{OH})_3$, 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 to remove the coat from aluminum surfaces and the coat adhering to the surface of a jig. As a result, waste sulfuric acid is produced. This waste sulfuric acid generally comprises 75 to 95% of free H_2O and 2 to 0.5% of $\text{Al}_2(\text{SO}_4)_3$.

In order to prevent environmental pollution and to preserve resources, the sludge and the waste sulfuric acid rising from aluminum surface treatment operations are generally used to prepare an aqueous aluminum sulfate solution. The reaction involved in the synthesis of aluminum sulfate, however, proceeds so quickly as to render control of the reaction velocity difficult. Further, since the aluminum sulfate as a final product should have a pH to suit its end purpose,

the final pH of the synthesis liquid must be adjusted so as to equal the pH of the aluminum sulfate. Since this adjustment of the pH is difficult, it has been regarded as difficult to produce an aqueous aluminum sulfate solution by a continuous synthesis.

The synthesis of an aluminum sulfate solution from sludge has been heretofore carried out only as a batchwise process, which generally comprises charging an appropriate reaction vessel with a fixed amount of waste sulfuric acid and heating the contents of the vessel with a fixed amount of sludge being gradually supplied thereto.

In the above batch process the reaction vessel should be made of a highly corrosion-resistant material because the contents of the vessel comprise mainly highly concentrated waste sulfuric acid during the initial stages of the process. For example, vessels provided with a glass lining are commonly used for the synthesis. Such vessels have the disadvantages that they are expensive, entail difficult maintenance works of repair and inspection, and tend to break easily. Moreover, since the synthesis is carried out batchwise, the reaction vessel must be large, the driving power is proportionately large and the equipment as a whole occupies a large volume and floor area. Thus, the synthesis involves high equipment costs and the reaction

vessel cannot be easily expanded to increase capacity. Further, owing to the batchwise production, the synthesis has the disadvantage that the operation is complicated in procedure and inferior in efficiency and the synthesis vessel, which is heated by means of a jacket, will suffer from a gradual loss of thermal efficiency due to scaling and entail a high running cost.

Another waste material produced in an aluminum surface treatment operation is a dilute aqueous sulfuric acid solution containing aluminum sulfate (hereinafter briefly referred to as "sulfuric alum") which is formed during recovery of sulfuric acid from the electrolyte itself and constitutes a problematic by-product in addition to the sludge and waste sulfuric acid. To date, the aqueous sulfuric acid solution containing sulfuric alum has not been produced in appreciable quantities and, therefore, has been sufficiently dealt with by waste water treatment. In recent years, various methods for the treatment of electrolytes, such as a method using an ion-exchange resin and a method using diffuse transmission membranes, have progressed. Owing to the advance of these methods, the aqueous sulfuric acid solution containing the sulfuric alum is rapidly increasing 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 anodic oxidation or 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, the 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 to keep pace with the improvement of quality of the aluminum surface treatment, this dilute aqueous sulfuric acid solution has been growing in volume. In the circumstances, the safe dispersal of the dilute aqueous sulfuric acid solution has proved a severe problem to the industry.

The acid solution might be used in the batchwise synthesis of aqueous aluminum sulfate solution. Indeed, the present applicants partially utilize the solution for the synthesis. However, since the 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.

It is an object of the invention to provide a continuous process for the production of an aqueous aluminum sulfate solution by effective use of the sludge, waste sulfuric acid, and sulfuric aluminum-containing aqueous aluminum sulfate solution arising in aluminum surface treatment operations.

According to one embodiment of the invention there is provided a method for the continuous production of an aqueous aluminum sulfate solution from by-products arising from aluminum surface treatment, namely (i) an aluminum sludge comprising mainly aluminum hydroxide, (ii) waste sulfuric acid arising during the removal of coatings in the surface treatment operation, and (iii) an aluminum sulfate-containing aqueous sulfuric acid solution arising during the recovery of sulfuric acid in the surface treatment operation; which method comprises feeding the sludge, waste sulfuric acid and aluminum sulfate-containing sulfuric acid to a reactor comprising a plurality of reaction vessels so that material fed tend to flow sequentially through the vessels from the first vessel to the last vessel to undergo reactions at

temperatures of 80°C to the boiling point of the reaction solution, and in which method part of the aluminum sulfate-containing aqueous sulfuric acid solution is fed to at least one of the vessels subsequent to the first, and the pH of the reaction solution in the last vessel is adjusted to a value of from 1.6 to 2.5.

In the method of the invention, the adjustment of the pH value of the reaction solution is an important factor for efficient continuous synthesis. In accordance with the present invention, therefore, there is also provided apparatus for the continuous production of an aqueous aluminum sulfate solution, which apparatus is designed so that adjustment of the pH value may be effected properly. This apparatus comprises a reactor comprising a plurality of sequentially connected reaction vessels adapted to permit continuous reactions of aluminum sludge, waste sulfuric acid and an aluminum sulfate-containing aqueous sulfuric acid solution;

a first feed conduit for feeding the aluminum sulfate-containing aqueous sulfuric acid solution to the first reaction vessel, a further feed conduit for feeding the aluminum sulfate-containing aqueous sulfuric acid solution to at least one reaction vessel subsequent to the first reaction vessel,

a first pH indicator-controller-recorder disposed inside the first or second reaction vessel,

a first control valve in connection with first pH indicator-controller-recorder and adapted to control the rate of flow in the first feed pipe,

a further pH indicator-controller-recorder disposed in at least one of the reaction vessels subsequent to the first reaction vessel, and

a further control valve in connection with the further pH indicator-controller-recorder and adapted to control the rate of flow within the further feed pipe.

Further in the method of the invention, the control of the temperature of the reaction solution is also an important factor for efficient continuous synthesis. In accordance with a further embodiment of the invention, therefore, there is provided an apparatus for reaction temperature control designed to permit continuous production of an aqueous aluminum sulfate solution from the above mentioned by-products, which apparatus comprises a reaction comprising sequentially connected reaction vessels,

a first heat exchanger for effecting exchange of heat between (a) the final aqueous aluminum sulfate solution from the reaction having a boiling point approximating the boiling point of the reaction solution and (b) the aluminum sulfate-containing aqueous sulfuric acid solution,

a first steam pipe disposed inside the first reaction vessel,

a first temperature indicator-controller-recorder disposed inside the first reaction vessel,

a first temperature control valve operating connected with the first temperature indicator-controller-recorder and adapted to control the flow of steam within the first steam pipe.

a further steam pipe and a further temperature indicator-recorder disposed inside at least one of the reaction vessels subsequent to the first reaction vessel, and

a further temperature control valve connected with the further temperature indicator-recorder and adapted to control manually or automatically the flow of steam within the further steam pipe.

In the following description reference will be made to the accompanying drawings in which:-

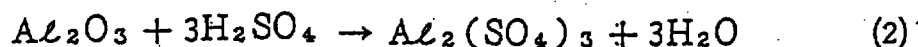
Fig. 1 is a flow sheet schematically illustrating a typical apparatus adapted to the continuous synthesis of an aqueous aluminum sulfate solution according to the present invention;

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

Fig. 3 is a partial longitudinal cross section through another form of reaction usable in the apparatus according to the present invention.

In the present invention, an aqueous aluminum sulfate solution is continuously synthesized by causing aluminum sludge, waste sulfuric acid and an aluminum sulfate-containing aqueous sulfuric acid solution (each produced in the surface treatment of aluminum) to react sequentially in a plurality of reaction vessels. The synthetic aluminum sulfate solution obtained at the end of these reactions is subjected to filtration and concentration to give aluminum sulfate as a finished product. The attributes of the finished product depend on the final pH of the synthetic aluminum sulfate solution and are regulated in a fixed range suitable for a particular purpose for which the finished product is to be used. In the present invention, the sulfuric alum-containing dilute aqueous sulfuric acid solution is utilized to adjust the pH value of the reaction solution.

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



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
$\text{Al}(\text{OH})_3$	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%
$\text{Al}_2(\text{SO}_4)_3$		0.6%	8.7%

Since the reaction of the aforementioned three materials was experimentally demonstrated to be regarded as a homogenous second order reaction, the velocity constant of the reaction was determined by a batch test. From the results of the test, it is found that the velocity constant at 90° to 100°C was 0.12 ~ 0.671 $\text{l}/\text{Al}_2\text{O}_3 \cdot \text{mol} \cdot \text{sec}$. 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 $\text{l}/\text{Al}_2\text{O}_3 \cdot \text{mol} \cdot \text{sec}$. In view of commercial operation of the synthesis, the highest permissible limit of the velocity constant is 2.0 $\text{l}/\text{Al}_2\text{O}_3 \cdot \text{mol} \cdot \text{sec}$.

If the pH value is unduly high, namely the amount of free
5 H_2SO_4 is unduly 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
10 manner that the pH value of the reaction solution in the first vessel in the compound of reaction vessels will be lowered to heighten the reaction velocity and the pH values of the reaction solutions in the subsequent vessels will be gradually increased sequentially to adjust the final pH value of the synthetic solution eventually to
15 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) reactor
20 having the component stages provided with respectively fixed volumes commensurate with the intended volumes of treatment at respectively 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
25 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 reactor. 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 vessels 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 vessel 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 reactor 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 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 conveyor 1 to the
5 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
10 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 exchange of heat with steam possessing a temperature of boiling
15 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
20 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
25 screen 16 disposed inside the receiving tank 15, and then forwarded to the first reaction tank R_1 by a pump 17.

In the reactor 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.

5 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
10 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
15 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
20 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
25 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 acid solution 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-controller-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
5 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 for the second and subsequent tanks.

Then, as regards the control of the temperature of the
10 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
15 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
20 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.
25 When the temperature so detected is below the prescribed level, a steam control valve 27 disposed in a steam feed pipe 2 and 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 controlling the amount of steam entering the second heat exchanger 7, the temperature is automatically controlled to the prescribed level. To the
5 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 led 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
10 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
15 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
20 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
25 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

5 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
10 and the reaction solution as illustrated 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
15 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
20 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
25 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 - $\text{Al}(\text{OH})_3$ 9.5% by weight

5 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

10 $\text{Al}_2(\text{SO}_4)_3$ 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

15 $\text{Al}_2(\text{SO}_4)_3$ 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

20 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. 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 reactor 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 reactor 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 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
5 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
10 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
15 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
20 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
25 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.

5 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
10 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
15 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
20 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
25 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.

5 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
10 coupled with the effect of continuous operation, the apparatus enjoys high energy efficiency and low power consumption and a low running cost as well.

CLAIMS:

1. A method for the continuous production of an aqueous aluminum sulfate solution from by-products occurring in aluminum surface treatment operations, namely (i) an aluminum sludge comprising mainly aluminum hydroxide, (ii) waste sulfuric acid and (iii) an aluminum sulfate-containing aqueous sulfuric acid solution, which method comprises feeding the sludge, waste sulfuric acid and aluminum sulfate-containing sulfuric acid to a reactor comprising a plurality of successively connected reaction vessels, causing the fed substances to flow sequentially through the vessels from the first vessel to the last vessel to undergo reactions at temperatures of from 80°C to the boiling point of the reaction solution; in which method a part of the aluminum sulfate-containing aqueous sulfuric acid solution is fed to at least one reaction vessel subsequent to the first reaction vessel, and the pH of the reaction solution in the last reaction vessel is adjusted to be from 1.6 to 2.5.

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



3. A method according to claim 2, wherein part of the aqueous aluminum sulfate solution from the final reaction vessel is returned to the first reaction vessel.

4. A method according to any one of the preceding claims wherein the pH of the reaction solution in the first or second reaction vessels is adjusted to be from 0.1 to 2.0

5. A method according to claim 4, wherein the adjustment of the pH of the reaction solution is effected by controlling the amount of aluminum sulfate-containing aqueous sulfuric acid solution fed to the first reaction vessel.

6. A method according to any one of the preceding claims wherein control of the temperature of the reaction solution in the reactor is effected by feeding steam to the reaction solution.

7. A method according to any one of claims 1 - 5, wherein the control of the temperature of the reaction solution in the reactor is effected by heat exchange between the reaction solution and a steam pipe immersed in the reaction solution.



8. A method according to any one of the preceding claims wherein the aluminum sulfate-containing aqueous sulfuric acid solution heated to an elevated temperature is fed to the first reaction vessel.

9. A method according to claim 1 substantially as hereinbefore described.

10. Apparatus when used for the continuous production of an aqueous aluminum sulfate solution from by-products arising from aluminum surface treatment by a method as claimed in claim 1, which apparatus comprises: a reactor comprising a plurality of successively connected reaction vessels to permit continuous reaction of an aluminum sludge comprising mainly aluminum hydroxide, waste sulfuric acid and an aluminum sulfate-containing aqueous sulfuric acid solution (all arising from aluminum surface treatment operations),

a first feed pipe for feeding aluminum sulfate-containing aqueous sulfuric acid solution to the first reaction vessel,

a further feed pipe for feeding aluminum sulfate-containing aqueous sulfuric acid solution to at least one reaction vessel subsequent to the first reaction vessel,

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



a first control valve operations connected with the first pH indicator-controller-recorder and adapted to control the flow rate within the first feed pipe,

a further pH indicator-controller-recorder disposed in at least one reaction vessel subsequent to the first reaction vessel, and

a further control valve operating connected with the further pH indicator-controller-recorder and adapted to control the flow volume within the further feed pipe.

11. Apparatus according to claim 10 in which the further feed pipe serves to feed aluminum sulfate-containing aqueous sulfuric acid solution to the reaction vessel immediately preceding the last reaction vessel, the further pH indicator-controller-recorder being disposed in the last reaction vessel.

12. Apparatus according to claim 10 or claim 11, wherein the reactor is divided into the plurality of reaction vessels by means of bulkheads suspended from above so as to form an opening on the bottom part of said reaction tank, and/or by weir-like bulkheads so as to allow overflow of the reaction solution.

15. Apparatus according to claim 12, wherein a baffle plate adapted to prevent short pass of the reaction solution is disposed in at least one of the reaction vessels.



14. Apparatus as claimed in claim 10 substantially as hereinbefore described with reference to the accompanying drawings.

15. Apparatus when used for reaction temperature control to permit continuous production of an aqueous aluminum sulfate solution from by-products produced in aluminum surface treatment by a method as claimed in claim 1, which apparatus comprise:

a react or comprising a plurality of successively connected reaction vessels adapted to permit continuous reaction of an aluminum sludge comprising mainly aluminumhydroxide, waste sulfuric acid and an aluminum sulfate-containing aqueous sulfuric acid (all arising from aluminum surface treatment operations),

a first heat exchanger for effecting heat exchange between (a) the final aqueous aluminum sulfate solution emanating from the reactor and having a boiling point approximating the boiling point of the reaction solution and (b) the aluminum sulfate-containing aqueous sulfuric acid solution,

a first steam pipe disposed inside the first reaction vessel,

a first temperature indicator-controller-recorder disposed inside the first reaction vessel,

a first temperature control valve operatively connected with the first temperature indicator-controller-recorder and adapted to control the flow of



steam within the first steam pipe.

a further steam pipe and a further temperature indicator-recorder disposed inside at least one of the reaction vessels subsequent to the first reaction used.

a further temperature control valve connected with the further temperature indicator-recorder and adapted to control manually or automatically, the flow of steam within the further steam pipe.
