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(54) PROCESS OF PRODUCING SULFURIC ACID FROM WASTE ACID AND IRON SULFATE

(71) We, METALLGESELLSCHAFT AKTIENGESELLSCHAFT, a body corporate organised under the Laws of the German Federal Republic, of 14 Reuterweg, Frankfurt am Main 6000, German Federal Republic and BAYER AKTIENGESELLSCHAFT, a body corporate organised under the Laws of the German Federal Republic, of 5090 Leverkusen, German Federal Republic, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:–

This invention relates to a process for producing sulfuric acid from waste sulfuric acid, which contains iron sulfate and has become available as a result of a solubilizing treatment of TiO_2-containing materials with sulfuric acid.

The solubilizing treatment of TiO_2-containing raw materials with sulfuric acid results in waste products which consist of waste sulfuric acid and, during the treatment of ilmenite, of the so-called green salt. Waste acid contains up to about 21% by weight of free sulfuric acid and metal sulfates, mainly iron sulfate. The solid green salt consists of ferrous sulfate having a high content of water of crystallization and contains up to about 90% by weight $FeSO_4.7H_2O$. A recovery of the raw materials is desirable for ecological reasons.

A direct processing of the green salt to effect a thermal dissociation into iron oxide and SO_2, which is processed to form sulfuric acid, is highly expensive because the dissociation must be effected at high temperatures and the high content of water of crystallization in the green salt must be heated to that temperature. Besides, the moisture must be removed from the released gases if they are to be subjected to dry catalysis.

Similar remarks are applicable to the processing of the waste acid by thermal dissociation because the sulfuric acid concentration is very low. For this reason the concentration of such waste acid is increased before it is dissociated.

It is known to conduct the waste acid which becomes available as a result of the solubilizing treatment of TiO_2-containing materials with sulfuric acid directly into the thickening zone of a crystallizer, in which concentrated sulfuric acid having a sulfuric acid concentration of 60-65% is added to increase the sulfuric acid concentration to 50-55%, and then to withdraw and filter off the ferrous sulfate, which has formed and settled and has a low content of water of crystallization, to treat the aqueous filtrate and the overflow effluent from the crystallizer, which contain 50-55% sulfuric acid, by means of an immersion burner in an evaporator to increase the sulfuric acid concentration to 60-65%, to conduct a partial stream of that acid of increased concentration into the crystallizer, and to increase the concentration of the other partial stream still further and then to re-use the latter partial stream for the solubilization of the TiO_2. The solid ferrous sulfate ($FeSO_4.H_2O$) which has been filtered off and has a low content of water of crystallization is then processed to form sulfuric acid (German Patent Specification 957,473). In that process, acid must be circulated at a very high rate in order that the mixing of the waste solid, which contains about 20% sulfuric acid, and of the more highly concentrated, circulated acid, which contains 60-65% sulfuric acid, results in mixed acids having a sulfuric acid concentration of 50-55%. Besides, solid green salt is not added to the process.

It is an object of the invention to provide an economical and ecologically satisfactory processing of the waste acid and of the solid ferrous sulfate, which has a high content of water of crystallization, which become available as a result of the solubilization of TiO_2.

According to the present invention there is provided a process for producing sulfuric acid from waste sulfuric acid, which contains ferrous sulfate and has become available as a result of a solubilizing treatment of titanium dioxide-containing material with sulfuric acid, comprising the steps of supplying heat to the waste acid: which is in the form of a suspension of hydrated metal sulfates in free sulfuric acid to increase its sulfuric acid concentration to 25 to 55%, based on the suspension, forming a mixture of the concentrated waste acid, filtrate produced subsequently in the process and having sulfuric acid concentration of 45 to 70% by weight, based on salt-free acid, and solid ferrous sulfate which has become available as a result of the solubilization of titanium dioxide and has a high content of water of crystallization, thereby to produce an acid mixture having a sulfuric acid concentration of 30 to 65% by weight, based on the first two components of the mixture, and thereby to transform the ferrous sulfate having a high content of water of crystallization to ferrous sulfate having a low content of water of crystallization, filtering the resulting suspension to provide a solid ferrous sulfate and an aqueous filtrate, thermally dissociating the solid ferrous sulfate which has been filtered off and has a low content of water of crystallization and the adhering sulfuric acid in a dissociation step, producing sulfuric acid from the sulfur dioxide-containing gases which are released in the dissociation step, supplying heat to the aqueous filtrate to increase its sulfuric acid concentration to 45 to 70% by weight, based on salt-free acid, and adding at least part of the filtrate of increased concentration to the waste acid.

The heat required to increase the concentration may be supplied by a direct and/or indirect transmission of heat. Low-grade heat, which becomes available at low temperatures, may be used on a large scale. The waste acid of increased concentration and aqueous filtrate of increased concentration are suitably mixed in a mixing stage or in the stage in which ferrous sulfate having a high content of water of crystallization is transformed to ferrous sulfate having a low content of water of crystallization. The solid ferrous sulfate having a high content of water of crystallization is suitably fed directly to that transforming stage. Any remainder of the filtrate of increased concentration is suitably used entirely or in part to solubilize the TiO_2. Alternatively, the remainder may be used entirely or in part for other purposes, such as the production of fertilizer or for other ore-leaching processes. The temperature must be selected so that previously formed ferrous sulfate having a low content of water of crystallization is not transformed back to ferrous sulfate having a high content of water of crystallization in the process, particularly during the filtration. The minimum temperature is 10 to 50°C, depending on the concentration of sulfuric acid, which should be 30 to 65%. Under these conditions, the transformation of ferrous sulfate having a high content of water of crystallization to ferrous sulfate having a low content of water of crystallization occurs automatically.

According to a preferred feature, at least part of the remainder of the filtrate of increased concentration is passed through the thermal dissociating stage before it is used to solubilize the TiO_2. As a result, the concentration of the acid is increased, as is required in the process, in such a manner that the dissociating stage is relieved.

The sulfuric acid concentration of the remainder of the filtrate which has been increased in concentration may be increased by an indirect supply of heat. This enables a further increase of the concentration of the acid to be achieved whereas a difficulty due to exhaust air does not arise.

The ratio of waste acid to solid ferrous sulfate having a high content of water of crystallization is preferably 0.5 to 0.9, more preferably 0.7. With a ratio in this range, part of the waste products of a TiO_2-recovering plant supplied with ilmenite can be treated by the present process with an allowance for the quantity of sulfuric acid which adheres to the filter cake consisting of ferrous sulfate having a low content of water of crystallization.

According to a preferred feature, the ratio of waste acid to solid ferrous sulfate having a high content of water of crystallization is 1.5 to 2.5. With a ratio in this range, all of the waste products of a TiO_2-recovering plant supplied with ilmenite can be treated by the present process.

The ratio of acid mixture to solid ferrous sulfate having a high content of water of crystallization is desirably at least 1 and preferably 2 to 3. A ratio in this range results also in desirable conditions with respect to the sulfuric acid adhering to the solid ferrous sulfate which has been filtered off and has a low content of water of crystallization as well as to the dissociation of said sulfuric acid and the salt content of the aqueous filtrate.

The sulfuric acid which adheres to the solid ferrous sulfate which has been filtered off and has a high content of water of crystallization preferably has a concentration of 30 to 60% by weight. This results in favorable operating conditions and in a relief of the dissociating stage.

This invention will be explained more fully with reference to Examples and to the accompanying drawing which is a flow scheme. For the sake of clearness, a separate acid-mixing stage is shown for the mixing of the acid. The solid ferrous sulfate having a high content of water of crystallization will be described as "green salt". The transformation of ferrous sulfate having a high content of water of crystallization into ferrous sulfate having a low content of water of crystallization will be described as "dehydration". In each of the Examples, sulfur dioxide-containing gases which are produced in a thermal dissociation stage are used to produce sulfuric acid. This is done in conventional manner (e.g. German Patent Specification 957,473 mentioned above) and need not be further described.

Example 1

As a result of the solubilizing treatment of Norwegian ilmenite with sulfuric acid, 4 tons of green salt and 8 tons of waste sulfuric acid become available per ton of TiO_2.

The green salt contains 90% by weight of $FeSO_4.7H_2O$ and 5% by weight adhering moisture, balance metal sulfate hydrates. The waste sulfuric acid has approximately the following chemical composition in % by weight:

$MeSO_4$	15
H_2SO_4	21
H_2O	64

where $MeSO_4$ denotes the sulfates of all metals, including iron, present in the waste sulfuric acid. At a rate of 8000 kg/h, the waste sulfuric acid in the form of a suspension of hydrated metal sulfates in free sulfuric acid is fed from supply tank 2 through conduit 2a to the strengthening stage 3, in which heat is supplied to the waste sulfuric acid to increase its concentration to 30.4% by weight H_2SO_4, based on the suspension. At a rate of 5520 kg/h, the suspension is fed through conduit 3a to an acid-mixing stage 4. At a rate of 4480 kg/h, additional waste acid containing 65% by weight H_2SO_4 is fed from a strengthening stage 8 to the acid-mixing stage. As a result, sulfuric acid having a concentration of 45.9% by weight is fed at a rate of 10,000 kg/h from the acid-mixing stage through conduit 4a to the dehydrating stage 5, which is also fed from a dump 1 through conduit 1a with green salt at a rate of 4000 kg/h. The dehydrating stage 5 is thus fed at a total rate of 14,000 kg/h and contains acid mixture and green salt in a ratio of 2.5:1. The resulting suspension has a sulfuric acid concentration of 32.8% by weight, based on the suspension, and contains about 230 g $MeSO_4$ per kg.

The suspension is filtered in a filtering stage 6. The resulting filter cake becoming available at a rate of 5200 kg/h contains $MeSO_4.H_2O$ as well as 30% by weight adhering sulfuric acid having an H_2SO_4 concentration of 44.3% and is fed to a dissociating stage 7 from which sulfur dioxide-containing gases are supplied to sulfuric acid producing plant (not shown).

The filtrate which becomes available at a rate of about 8800 kg/h is strengthened in the strengthening stage 8 from 44.3 to 65% by weight H_2SO_4 by a supply of heat.

Of the total rate of about 6000 kg/h, part of the filtrate, at a rate of 4480 kg/h, is fed through conduit 8a to the acid-mixing stage. The remainder, amounting to about 1520 kg/h and containing sulfuric acid at a rate of about 990 kg/h, may be used to solubilize the TiO_2. This rate corresponds to about 50% of the sulfuric acid content of the free sulfuric acid which is contained in the waste sulfuric acid.

The temperature in the filtering stage amounted to 40-50°C.

Example 2

The waste sulfuric acid and the green salt had the same compositions and were used at the same rates as in Example 1.

In the strengthening stage 3, the waste sulfuric acid was strengthened to 30.4% by weight of sulfuric acid. The suspension which became available at 5520 kg/h was mixed in the acid-mixing stage 4 with acid of 65% concentration supplied from the strengthening stage 8 at a rate of 480 kg/h. The resulting suspension becoming available at a rate of 6000 kg/h and having a sulfuric acid concentration of 33.1% by weight is fed to the dehydrating stage together with the green salt from 1. The resulting suspension at a rate of 10,000 kg/h had a sulfuric acid concentration of 19.9% by weight and contained 324 g metal sulfate per kg of the suspension. The ratio of acid mixture to green salt was 1.5:1.

When this suspension was filtered in 6, metal sulfate monohydrate and adhering sulfuric acid became available at a rate of about 5200 kg/h and were thermally dissociated in stage 7 to produce sulfur dioxide-containing gases. The filtrate became available at a rate of about 4800 kg/h and had a sulfuric acid concentration of 31.3% by weight and was strengthened in 8 to a concentration of 65% by weight. Of the resulting waste sulfuric acid which became available at a rate of about 2300 kg/h, a partial stream, at a rate of 480 kg/h, was fed to the acid-mixing stage and the remainder, having also a concentration of 65% by weight H_2SO_4, can be fed at a rate of about 1820 kg/h directly to the TiO_2-solubilizing stage. In this arrangement, about 70% of the free sulfuric acid contained in the waste acid can be directly recovered.

The temperature in the filtering stage amounted to 60-70°.

Example 3

The waste sulfuric acid and the green salt had the same compositions and were used at the same rates as in Example 1.

In stage 3, the waste sulfuric acid was strengthened to 40.8% by weight H_2SO_4, based on the suspension, by a supply of heat. The resulting suspension which became available at a rate of 4120 kg/h was fed to the acid-mixing stage 4, which was also fed from 8 with 65% waste sulfuric acid at a rate of 5680 kg/h so that a suspension became available at a total rate of 10,000 kg/h. This suspension from 4 and the green salt from 1 were fed to the dehydrating stage 5, where a suspension containing 39.4% by weight of H_2SO_4 and 230 g $MeSO_4$ per kg became available at a total rate of 14,000 kg/h.

As a result of the filtration in 6, a filter cake consisting of $MeSO_4.H_2O$ and about 30% by weight adhering sulfuring acid became available at a rate of 5200 kg/h and was thermally dissociated at this rate.

The filtrate containing 53% by weight H_2SO_4 became available at a rate of about 8800 kg/h and was strengthened to 65% by weight H_2SO_4 in the strengthening stage 8 by a supply of heat. Part of the resulting waste acid, at a rate of 5880 kg/h, was fed to the acid-mixing plant. The remainder, at a rate of 1300 kg/h, was directly fed to the TiO_2-solubilizing stage. The rate of the directly used sulfuric acid amounted to about 840 kg/h and corresponds to about 50% of the free sulfuric acid content of the waste sulfuric acid.

The temperature in the filtering stage was 30 to 40°C.

Example 4

In this arrangement, about 40% of the waste sulfuric acid which became available as a result of the TiO_2-solubilizing treatment, corresponding to a rate of 3300 kg/h, were processed. This rate corresponds to the rate at which sulfuric acid is lost due to the adhesion to metal sulfate monohydrates after the filtration. The rate of green salt, amounting to 4000 kg/h, and the composition are the same as in Example 1.

The waste sulfuric acid is first strengthened in 3 to 30.4% by weight H_2SO_4, based on the suspension. The resulting suspension which became available at a rate of 2280 kg/h is mixed in stage 4 with 65% waste sulfuric acid, which is fed from stage 8 at a rate of 7720 kg/h. As a result, a suspension having an H_2SO_4 concentration of 57.2% by weight became available at a rate of 10,000 kg/h and was used to dehydrate green salt at a rate of 4000 kg/h.

The resulting suspension which became available at a rate of 14,000 kg/h contained 40.8% by weight H_2SO_4 and 180 g metal sulfate per kg and was filtered in stage 6. A filter cake containing 30% by weight adhering sulfuric acid became available at a rate of 4100 kg/h and was fed to the dissociating stage 7 to produce sulfur dioxide containing gases. The filtrate which became available was strengthened to 65% by weight H_2SO_4 and at the total rate of 7720 kg/h was fed to the acid-mixing stage 4.

The temperature in the filtering stage was 40-50°C.

The advantages of the invention reside mainly in that the salt-containing waste acid and the iron sulfate having a high content of water of crystallization which become available can be processed with a relatively low expenditure and in an ecologically satisfactory manner in a process in which waste products are not obtained at all in some cases whereas the resulting raw materials can be used entirely in the same process or partly in other processes so that waste products are not obtained. Even when part of the strengthened filtrate must be discarded because it cannot be used, a large part of the waste materials are processed and re-used in an ecologically satisfactory manner.

WHAT WE CLAIM IS:

1. A process for producing sulfuric acid from waste sulfuric acid, which contains ferrous sulfate and has become available as a result of a solubilizing treatment of titanium dioxide-containing material with sulfuric acid, comprising the steps of supplying heat to the waste acid which is in the form of a suspension of hydrated metal sulfates in free sulfuric acid to increase its sulfuric acid concentration to 25 to 55%, based on the suspension, forming a mixture of the concentrated waste acid, filtrate produced subsequently in the process and having a sulfuric acid concentration of 45 to 70% by weight, based on salt-free acid, and solid ferrous sulfate which has become available as a result of the solubilization of titanium dioxide and which has a high content of water of crystallization, thereby to produce an acid mixture having a sulfuric acid concentration of 30 to 65% by weight, based on the first two components of the mixture and thereby to transform the ferrous sulfate having a high content of water of crystallization to ferrous sulfate having a low content of water of crystallization, filtering the resulting suspension to provide a solid ferrous sulfate and an aqueous filtrate, thermally dissociating the solid ferrous sulfate which has been filtered off and has a low content of water of crystallization and the adhering sulfuric acid in a dissociation step, producing sulfuric acid from the sulfur dioxide-containing gases which are released in the dissociation step, supplying heat to the aqueous filtrate to increase its sulfuric acid concentration to 45 to 70% by weight, based on salt-free acid, and adding at least part of the filtrate of increased concentration to the waste acid.

2. A process as claimed in Claim 1, wherein at least part of the remainder of the filtrate of increased concentration is passed through the thermal dissociating stage before it is used to solubilize the titanium dioxide.

3. A process as claimed in Claim 1 or 2, wherein the sulfuric acid concentration of the remainder of the filtrate of increased concentration is increased by the indirect

supply of heat to said filtrate.

4. A process as claimed in any one of Claims 1 to 3, wherein the ratio of waste acid to solid ferrous sulfate having a high content of water of crystallization is 0.5 to 0.9.

5. A process as claimed in any one of Claims 1 to 4, wherein the ratio of waste acid to solid ferrous sulfate having a high content of water of crystallization is 0.7.

6. A process as claimed in any one of Claims 1 to 3, wherein the ratio of waste acid to solid ferrous sulfate having a high content of water of crystallization is 1.5 to 2.5.

7. A process as claimed in any one of Claims 1 to 6, wherein the ratio of acid mixture to solid ferrous sulfate having a high content of water of crystallization is at least 1.

8. A process as claimed in any one of Claims 1 to 7, wherein the ratio of acid mixture to solid ferrous sulfate having a high content of water of crystallization is from 2 to 3.

9. A process as claimed in any one of Claims 1 to 6, wherein the sulfuric acid which adheres to the solid ferrous sulfate which has been filtered off and has a high content of water of crystallization has a concentration of 30 to 60% by weight.

10. A process for producing sulfuric acid from waste sulfuric acid substantially as hereinbefore described in any one of the foregoing Examples.

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1585535 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*