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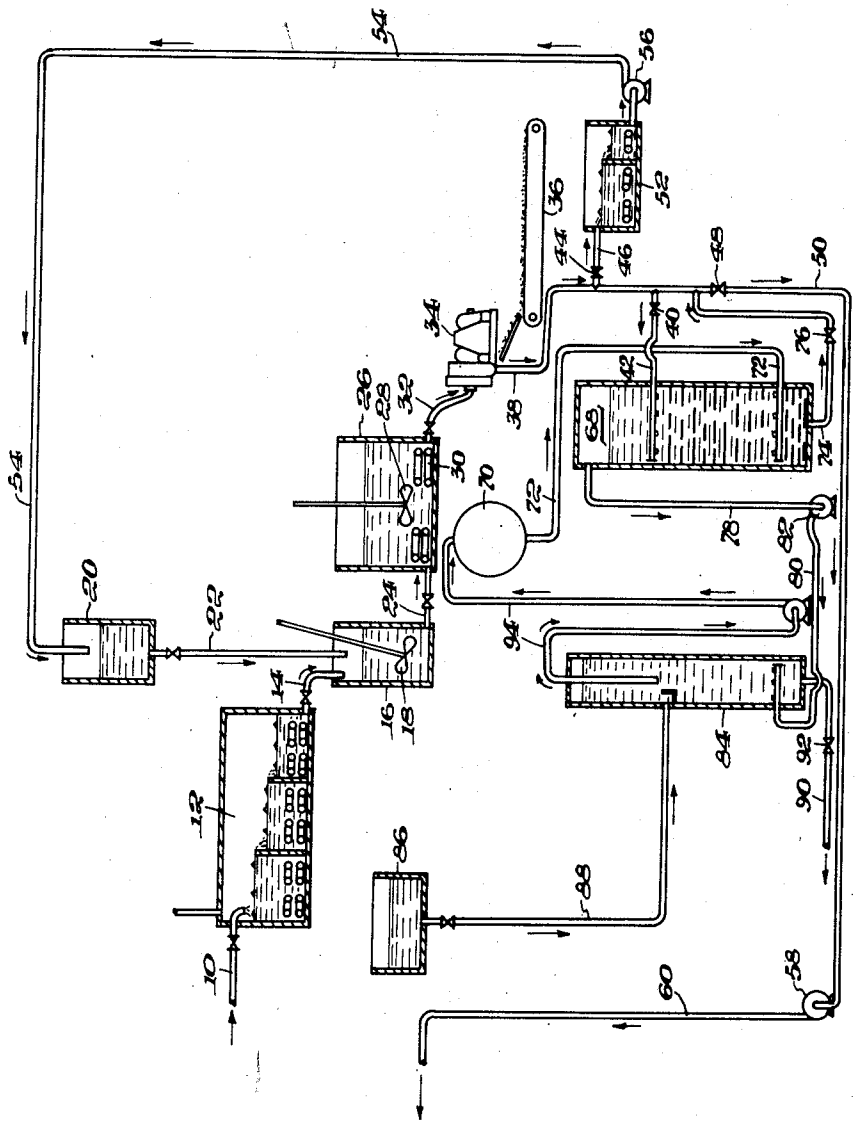

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REGENERATION OF SPENT PICKLE LIQUOR AND RECOVERY OF FERROUS SULFATE MONOHYDRATE

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1

The present invention relates to the regeneration of spent pickle liquor which has been employed in the cleaning or pickling of iron or steel or like metal articles, and which constitutes substantially a mild sulfuric acid solution of ferrous sulfate.

The enormous quantities of spent pickle liquor which are produced in industry and the magnitude of the problem of its disposal or utilization are well known. To meet the problem of disposal of these corrosive and acidic liquors many processes have been developed for reclamation of the waste liquors, the extraction of the iron content, and the recycling of regenerated liquor. Such processes, although furnishing partial solutions for this considerable problem, have not swept the industry because each of them is subject to one or more disadvantages, particularly one of the following: the costly need for evaporating large quantities of water often under the disadvantageous condition of precipitating a difficultly manageable slurry, the necessity of handling and circulating sulfuric acid solution of highly corrosive concentrations, and the circumstance of precipitating a large proportion, if not all, of the iron in the waste liquors as copperas, $FeSO_4.7H_2O$, a salt which can be treated only with difficulty for recovery of its sulfur in the regeneration of the acid for recycling to the pickling baths.

It is a primary object of the present invention to provide a process for the regeneration of waste pickle liquor that is simple and easy to operate, in which evaporation costs are kept at a minimum, and in which the recovered iron is obtained as ferrous sulfate monohydrate from which sulfuric acid can be readily regenerated.

It is another object of the present invention to provide a novel process for regeneration of waste pickle liquors in which all of the above-mentioned objects are obtained and in which, in addition, the acid concentrations are so regulated that the acidic solutions can be handled, without danger of corrosion in commonly used stainless alloy metals used for handling sulfuric acid solutions.

Another object of the present invention is the provision of a process wherein both the free and combined sulfuric acid content of spent liquor is recovered in sufficiently pure form that it can be used not only in further pickling operation but can also be used in other associated processes, in particular, in the ammonia saturator of a by-product coke plant.

The invention has for further objects such other improvements and such other operative advantages or results as may be found to obtain in the processes or apparatus hereinafter described or claimed.

2

Briefly stated, the present invention comprehends an improved process of regenerating spent pickle liquor wherein the pickle liquor is, after removal from the pickling baths, evaporated to a point at which the salts therein predominantly ferrous sulfate, are just short of the saturation point, then adding strong sulfuric acid to the hot concentrated liquor and permitting the mixture to cool to thereby precipitate all but traces of the ferrous sulfate monohydrate which can be readily smelted for recovery of sulfur oxygen gases therefrom. The filtrate from the filtration of the monohydrate can be concentrated, in whole or in part, and a concentrated portion returned to the regeneration process or all can be returned directly to the pickling baths or other uses. In case it is observed that some accumulation of extraneous impurities exists therein, the filtrate can be treated with an organic solvent such as benzene whereby the filtrate is clarified and purified. In those instances where it is found desirable to add fresh acid to the pickling process, the regenerated acid can be utilized in the ammonia saturator of a by-product coke plant, which plants are usually, for obvious purposes, found closely adjacent pickling operations. The regenerated acid obtained by the process provides in saturator operation an ammonium sulfate of good quality. It has in the past been recognized that it is advantageous to add sulfuric acid to waste pickle liquor before removal of the salt therefrom but as such previous additions have been performed without intermediate evaporation of the solution, the precipitation of large quantities of copperas has resulted as otherwise in feasibly large volumes of acid would have been acquired and produced. Separation of salt by evaporation alone has resulted also in precipitation of copperas.

It has been found in the development of the present process that, while the character of the ferrous sulfate monohydrate precipitation is primarily governed by the acid strength and the salt concentration of the mother liquor, a delay is usually beneficial in removing the last traces of the salt. Minute traces of the salt continue to crystallize out of the mother liquor over a period of many days yielding an improved regenerated acid, probably in accordance with obscure and little understood laws of crystallization. A delay period of three hours will be long enough to produce a recovered acid of sufficient purity for most

purposes, but where necessary the acid can be allowed to stand a longer time to achieve more rigid standards of purity.

The evaporation of the waste pickle liquor down to only its saturation concentration and the combination therewith of subsequent regeneration steps are so arranged that only about 85% of the water of the waste pickle liquor need be evaporated.

As is well known, the acid strength of waste pickle liquor is low. After the liquor has been concentrated in the present process, a sufficient quantity of strong acid is added thereto that the acid concentration of the admixture is immediately raised above the range at which sulfuric acid is most corrosive. The present process employs solutions of acid concentration below 10% and above about 60%. Consequently, at no time need solutions of highly corrosive strength be transported in the system, and apparatus embodying the present process do not require the use of the more highly expensive alloys.

In the accompanying drawing forming a part of the specification the single figure is a schematic flow diagram of apparatus in which the process may be carried out.

In operation according to the present invention and as illustrated by the aforesaid flow diagram, 1,000 gallons of spent pickle liquor is flowed through valved pipe **10** into a step-wise evaporator **12** wherein water of approximately 50% to 60% by volume of the pickle liquor is evaporated therefrom. Substantially no precipitation of salts occurs in the said evaporator **12** because evaporation is not carried beyond the concentration at which saturation is reached. The approximately 400 gallons of concentrate is flowed without substantial cooling through a valved pipe **14** into mixing tank **16** having agitator means **18**. Substantially an equal volume of 95% sulfuric acid is added to the concentrate from a storage tank **20** through valved pipe **22**. The concentrate, which has been brought to an acid concentration of 63% to 70% by weight, is flowed from the mixing tank **16** through a valved pipe **24** into a cooling and mixing tank **26** having agitator means **28** and cooling coils **30**. The acidified solution is cooled therein for a period of three hours, during which period the solution is brought to a temperature of about 25° C. During said cooling a considerable mass of crystals is precipitated therefrom. After cooling the so-formed slurry is flowed through a valved pipe **32** into a centrifuge **34** by which means salt, constituting ferrous sulfate monohydrate is separated, which salt contains about 28 gallons of water as water of constitution. The salt also retains approximately 40% of its own weight of mother liquor.

The monohydrate is carried on the belt conveyor means **36** to storage or to smelting equipment whereby the monohydrate can be readily converted into iron oxide suitable for the blast furnace. The iron oxide is in easily pulverizable form so that it may be also used for many other purposes. Liberated sulfur dioxide from said ferrous sulfate smelting can be converted by the well known sulfuric acid processes to 100% sulfuric acid, of which in this example 84 gallons can be obtained. The so-obtained sulfuric acid can be returned to storage tank **20** for use in regeneration of further quantities of spent pickle liquor or it can be otherwise used.

Mother liquor obtained from the separation in centrifuge **34** is flowed from a pipe **38** and by operation of valves **40** in pipe **42**, valve **44** in pipe **46** or valve **48** in pipe **50** can be flowed either exclusively or partly through one or more of three apparatus for its further treatment. Mother liquor flowing through pipe **46** flows into an evaporator **52**. In the example above described a mother liquor of 630 gallons is obtained. The mother liquor has a sulfuric acid concentration of 63% to 70% and contained only about 0.040% iron by weight. By evaporation in the said evaporator **52**, 223 gallons of water may be removed to raise the acid strength to about 95%. The 95% sulfuric acid is pumped through line **54** by the pump **56** into the said storage tank **20** wherein it is stored for use in regenerating further quantities of spent pickle liquor.

If desired, the mother liquor, which contains only about 0.040% iron by weight and has a 63% acid concentration, can be pumped by pump **58** through lines **50** and **60** directly to the pickling baths (not shown). The accumulation of impurities, such for example, as inhibitors employed in the pickling process and organic compounds released by the action of acid on steel, is indicated by the coloring of the mother liquor leaving the centrifuge **34**. Such colored mother liquor is flowed through valved pipe **42** into the upper end of a scrubbing column **68** wherein the acid is scrubbed with a countercurrent flow of benzol introduced from a storage tank **70** through a pipe **72** into the said column near the bottom thereof. Washed mother liquor settles to the bottom of the column, is drained through a line **74** having a valve **76** into pipe **50**, and is pumped by the said pump **58** through the line **60** to the pickling baths (not shown). After treatment of the mother liquor, benzol is decanted from the tower **68** through a pipe **78** and is pumped through a pipe **80** by pump **82** into a caustic cleaning tank **84** within which the benzol is caused to pass through a static column of caustic soda solution. At intervals caustic soda solution is renewed from storage **86** through a pipe **88** and used caustic solution is drained through pipe **90** by operation of valve **92** and can be directed to such use, for example, as neutralizing wash water used after the pickling operation. Washed benzol is pumped from the tank **84** through a pipe **94** to the storage tank **70**. A second washing tank can be disposed in parallel to tank **84** for use during replenishment of the latter tank.

The foregoing procedure provides substantially complete regeneration of spent pickle liquor so that, aside from make-up for losses, no addition of fresh sulfuric acid is required.

The following examples are presented for the purpose of illustrating the present invention.

Example 1

A waste pickle liquor having an analysis as follows:

Sp. Gr. 25°/25° C	1.179
$FeSO_4$	143 grams per liter
Free H_2SO_4	70 grams per liter
Ferric sulfate	5.3 grams per liter

was distilled and approximately 316 parts by weight of water were removed from an original quantity of 699.2 parts by weight of the pickle liquor. 380.3 parts by weight of 95% sulfuric acid were added to the hot distillation residue. This mixture was cooled and allowed to stand

and thereafter was filtered. The filter cake constituted ferrous sulfate monohydrate plus a small amount of mother liquor. The filtrate contained only 0.074% total iron and constituted 69.4% sulfuric acid and therefore was effectively regenerated.

Example 2

Another portion, in this instance 585 parts by weight, of the aforesaid spent pickle liquor, was evaporated to the extent that 325 parts by weight of water were removed. 192 parts by weight of 95% sulfuric acid were added to the hot evaporation residue. The mixture was allowed to cool and was subsequently filtered. The filtrate comprised regenerated acid containing 58.66% sulfuric acid and contained only 0.082% iron. The filter cake consisted of ferrous sulfate monohydrate and a small amount of mother liquor.

Example 3

A spent pickle liquor having the following analysis:

Sp. Gr. 25°/25° C	1.237
Ferrous sulfate	230 grams per liter
Ferric sulfate	7.8 grams per liter
$MnSO_4$	trace
H_2SO_4	36 grams per liter

was evaporated so as to remove 121 parts by weight of water from an original sample of 247.4 parts by weight. 118.6 parts by weight of 96.5% sulfuric acid were added to the hot residue. The mixture was allowed to stand and was subsequently filtered. The filtrate comprised regenerated sulfuric acid containing 62.66% sulfuric acid and only 0.057% total iron. Again the filtered cake constituted substantially only ferrous sulfate monohydrate and some mother liquor.

Example 4

A further quantity of the spent pickle liquor employed in the preceding example was evaporated, so that 122 parts of water were removed by distillation from 247.4 parts by weight of the pickle liquor. 102 parts by weight of 96.5% sulfuric acid were added. The mixture was cooled and allowed to stand and was then filtered. The filtrate comprised regenerated acid of 59.22% strength and contained only 0.112% total iron. The filter cake was ferrous sulfate monohydrate plus a small amount of mother liquor.

Example 5

A portion of the waste pickle liquor employed in Example 3 and constituting 741 parts by weight was evaporated so as to remove 368 parts by weight of water. 355.8 parts by weight of 96.5% sulfuric acid were added to the hot residue. The mixture was cooled, allowed to stand and then filtered. The filtrate constituted regenerated acid containing 63.48% sulfuric acid and only 0.054 total iron. The filter cake comprised ferrous sulfate monohydrate plus a small amount of mother liquor, the acid of which is, of course, made available for recycling to the pickling operation when the acid is recovered from the ferrous sulfate monohydrate.

The ferrous sulfate monohydrate obtained in the foregoing examples can be readily roasted for recovery of its sulfur in the form of strong sulfuric acid. The ferrous sulfate slurry obtained in the foregoing example filtered readily and comprised a heavy grey solid of sandy texture which did not melt upon roasting.

Pickle liquors described above which contain less than 10% concentration by weight of sulfuric acid or liquors which contain more than 63% and preferably more than 65% concentration by weight of sulfuric acid may be safely handled in the commonly used stainless steel alloy equipment. Such pickle liquors of maximum and minimum acid strengths respectively are substantially non-corrosive to the less expensive stainless alloys such as the austentitic stainless steels. The stainless steel which contains 18% chromium and 8% nickel is the least expensive of a group of other austenitic stainless steels which contain more than 18% chromium and 8% nickel. These latter alloys also generally contain other metals, such as molybdenum and vanadium. The corrosiveness of pickle liquor to 18 and 8 stainless steel gradually increases as the acid strength increases from 0 to 10% strength, is very corrosive for acid strengths between 10% and 60% sulfuric acid concentration, and decreases rapidly as the acid strength increases above 65% sulfuric acid.

The corrosiveness of pickle liquors having sulfuric acid strengths between 10% and 60% is less to austenitic stainless steels which contain more than 18% chromium and 8% nickel. A stainless alloy which is composed of roughly 88% cast iron and 12% silica (known as Duriron) is corrosive-resistant to a pickle liquor of substantially any strength of sulfuric acid. Another stainless alloy composed roughly of one-third copper and two-thirds nickel (known as Monel metal) is corrosive-resistant to pickle liquor having a sulfuric acid strength from 0 to 70%. The ordinary 18 and 8 stainless steel, Monel metal and Duriron are relatively inexpensive and preferably may be used with the pickle liquor of the present invention.

This application is a continuation in part of my application Serial No. 779,108, filed October 10, 1947, for Regeneration of Spent Pickle Liquor, now abandoned.

The invention as hereinabove set forth is embodied in particular form and manner but may be variously embodied within the scope of the claims hereinafter made.

I claim:

1. The method of separating into ferrous sulfate and concentrated sulfuric acid pickle liquor that contains less than 10% by weight of sulfuric acid and has been produced by treating ferrous metal with sulfuric acid, said method comprising in combination the steps of: concentrating said pickle liquor in the absence of copperas to substantially 50% to 60% of its volume by evaporation and without substantial precipitation of ferrous sulfate monohydrate therefrom; thereafter adding concentrated sulfuric acid to said evaporated liquor to produce an aqueous mixture containing at least 63% to 70% by weight of sulfuric acid; cooling said aqueous mixture to approximately 25° C. to precipitate substantially all of the iron in the solution as ferrous sulfate monohydrate; separating the so-precipitated monohydrate of ferrous sulfate from said acid liquor and evaporating water from so-separated liquor in a vessel of acid-resisting alloy to a concentration of sulfuric acid suitable for use in pickling liquor for ferrous metal.

2. In a method of regenerating spent pickle liquor remaining from the sulfuric acid treatment of ferrous metal so as to recover from said liquor ferrous sulfate in the form of a monohydrate and to recover from said liquor, in the form of acid substantially free of ferrous sulfate,

the sulfuric acid present in said liquor, the combination of steps which comprises: removing by evaporation in the absence of copperas from a quantity of spent liquor of as much water as can be removed without precipitation of solids to thereby reduce the volume of said quantity of liquor on the order of at least 50%, adding a sufficient quantity of concentrated sulfuric acid to the evaporated liquor to precipitate upon cooling the ferrous sulfate therein as an easily filtrable monohydrate, the concentration and quantity of acid added being such as to produce a solution having an acid concentration of 63% to 70% H_2SO_4 to thereby precipitate from said solution substantially all of the ferrous sulfate present therein in the presence of sulfuric acid of such high acid concentration as to be above the range in which it is highly corrosive to commonly used stainless alloys, separating the ferrous sulfate monohydrate from the solution by filtration and evaporating at least a portion of the resulting filtrate to remove water in such quantity as to provide a concentrated sulfuric acid and almost completely free of iron salts for recycling back to the step of precipitation of the ferrous sulfate monohydrate.

3. In a method of regenerating spent pickle liquor remaining from the sulfuric acid treatment of ferrous metal so as to recover from said liquor ferrous sulfate in the form of a monohydrate and to recover sulfuric acid present in the liquor in a concentration which is not highly corrosive to commonly used stainless alloys the combination of steps which comprises: removal by evaporation in the absence of copperas from a quantity of the spent liquor of as much water as can be removed without precipitation of ferrous sulfate, adding a substantially equal volume of concentrated sulfuric acid to the evaporated liquor to produce an acid concentration of 63% to 70% sulfuric acid, slowly cooling the solution to assist in the precipitation of ferrous sulfate monohydrate, filtering the solution to separate ferrous sulfate monohydrate from a regenerated pickle liquor filtrate having an acid concentration above 60% sulfuric acid which is not corrosive to commonly used stainless alloys, evaporating a portion of the filtrate to form concentrated sulfuric acid (at least 95% concentration) free of iron salts, and recycling the concentrated acid portion back to the process for precipitating ferrous sulfate monohydrate.

4. In a method of regenerating spent pickle liquor remaining from the sulfuric acid treatment of ferrous metal so as to recover from said liquor ferrous sulfate in the form of a monohydrate substantially free of copperas and to recover sulfuric acid present in the liquor in a concentration which is not highly corrosive to commonly used stainless alloys the combination of steps which comprises: removal by evaporation at atmospheric pressure from a quantity of the spent liquor of as much water as can be removed without precipitation of ferrous sulfate, adding concentrated sulfuric acid to the evaporated liquor to produce an acid concentration of 63% to 70% sulfuric acid, slowly cooling the solution to approximately 25° C. to assist in the precipitation of ferrous sulfate monohydrate, filtering the solution to separate ferrous sulfate monohydrate from a regenerated pickle liquor filtrate having a sulfuric acid concentration above 60% which is not corrosive to commonly used stainless alloys, evaporating a portion of the filtrate to form concentrated sulfuric acid (at least 95% concentration) free of iron salts, recycling the concentrated acid portion back to the process for precipitating ferrous sulfate monohydrate, and washing the regenerated pickle liquor with benzol to remove organic compound impurities therefrom before returning the pickle liquor to a pickling bath.

5. The method of separating into ferrous sulphate and sulphuric acid, pickle liquor that has been produced by treating ferrous metal with sulphuric acid, said method comprising in combination the steps of evaporating said pickle liquor until the same is saturated with respect to said ferrous sulphate but without any substantial crystallization of ferrous sulphate therefrom, thereafter adding sufficient concentrated sulphuric acid to said evaporated liquor to precipitate the iron in the solution as ferrous sulphate monohydrate and finally separating the so-precipitated monohydrate from said acid liquor.

6. The method of claim 5 wherein sufficient concentrated sulphuric acid is added to said liquor to produce a solution having an acidity in excess of about 50%.

7. The method of claim 6 wherein the evaporated liquor, after the addition of concentrated sulphuric acid thereto, is cooled to about 25° C. to aid in the precipitation of the monohydrate therefrom.

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