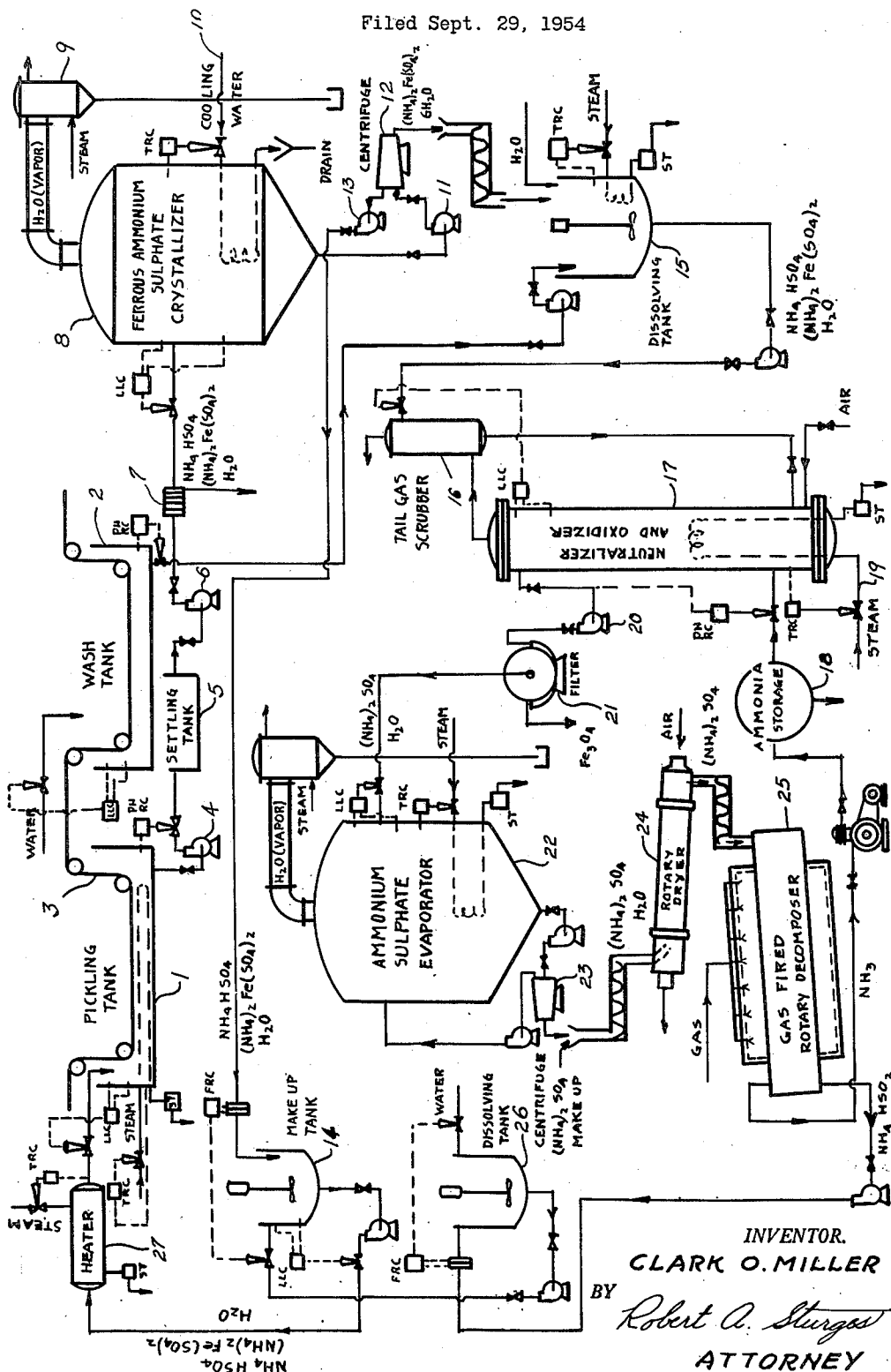


C. O. MILLER

METHOD OF PICKLING IRON AND RECOVERING PICKLING AGENT

Filed Sept. 29, 1954



1

2,769,735

METHOD OF PICKLING IRON AND RECOVERING PICKLING AGENT

Clark O. Miller, Cleveland, Ohio, assignor to Cleveland Industrial Research, Inc., Cleveland, Ohio, a corporation of Ohio

Application September 29, 1954, Serial No. 459,101

7 Claims. (Cl. 134-13)

This invention relates, as indicated, to an improved method of pickling ferrous metals and recovering the pickling agent.

In my prior application for patent, Ser. No. 368,049, filed July 15, 1953, now patent number 2,700,004 dated January 18, 1955, of which the present application is a continuation-in-part, there was disclosed a novel process for pickling iron. The present invention is an improvement upon my earlier process.

According to the earlier process, a ferrous metal is immersed in an aqueous pickling bath of ammonium acid sulphate to yield ferrous ammonium sulphate in aqueous solution. The concentration of ammonium acid sulphate may be anywhere within the range of 5% to 90% and most practically within the range of 10% to about 50%. Generally, the pickling bath is heated to a temperature of from 50° C. to 130° C., the more practical range being from about 80° C. to about 110° C. Normally, the time of exposure ranges from about 30 seconds to 20 minutes or more, depending on a great many production factors, and, of course, the extent of sealing, the temperature and the concentration of the bath. These factors also operate in the present sulphuric acid processes so that those skilled in the art of pickling steel will be readily able to familiarize themselves with the behavior of ammonium acid sulphate baths as it relates to the desired end result.

Thereafter, by a process including the steps of oxidation and raising the pH to at least 7 with an ammonia-containing fluid, e. g., ammonia gas or aqua ammonia, the ferrous ammonium sulphate is converted to oxide of iron (probably a ferrous-ferric oxide complex) and di-ammonium sulphate. The iron oxides precipitate out enabling recovery of di-ammonium sulphate. Di-ammonium sulphate, when heated, is converted to ammonium acid sulphate and ammonia, both of which products may be returned to the process, and no waste pickle liquor disposal problem is encountered.

It has now been found that the process is very materially improved through utilization of the discovery that ferrous ammonium sulphate in an aqueous solution of ammonium acid sulphate is easily crystallized out, for example, by moderate concentration and/or cooling, e. g., as by flashing.

If the concentration of ammonium acid sulphate is low to begin with, i. e., 5 to 15%, a larger portion of water must be evaporated before significant crystallization of ferrous ammonium sulphate is achieved. If the concentration of the pickling agent is very high (70-90%), it may even be necessary to add water to effect a cleaner separation of the ferrous ammonium sulphate. A very satisfactory initial concentration has been found to be about 35% to 40% NH_4HSO_4 in water. Nearly all the iron is precipitated as ferrous ammonium sulphate on cooling to room temperature from about 90° C. Relatively pure ferrous ammonium sulphate is removed from the solution for further processing.

The ammonium acid sulphate remaining in aqueous

2

solution, unreacted with iron and scale, is immediately re-circulated to the fresh pickle liquor make-up tank without being neutralized, evaporated and otherwise carried through the process. Less ammonia containing fluid is required for neutralization. These and other improvements of both chemical and economic considerations are effected by the employment of the ferrous ammonium sulphate crystallization step in the prior process.

Utilizing the improvements of the present invention, the size of the plant, i. e., the decomposer, the neutralization equipment, etc. may be nearly half the capacity which is required when this improvement is not employed. Under ordinary pickling conditions, only about $\frac{1}{2}$ the pickling acid is utilized before removal from the pickling bath. Thus, in the present case, only about $\frac{1}{2}$ the ammonium acid sulphate is converted to iron sulphate. By removing the iron sulphate and returning the balance of the unreacted ammonium acid sulphate to the pickling liquor make-up tank, only about $\frac{1}{2}$ of the amount of neutralization is required and the equipment is not involved in unnecessarily handling quantities of ammonium acid sulphate which have undergone no useful reaction. The reduction in the size of equipment occurs, of course, after the crystallizer. The size of the oxidizer, however, will be about the same in either case. The amount of ammonia utilized in neutralizing acidic liquors is, therefore, about $\frac{1}{2}$ of that ordinarily required.

It is a principal object of this invention, therefore, to improve the prior novel process in the manner indicated above.

Other objects will appear as the description proceeds. To the accomplishment of the foregoing and related ends, said invention, then, consists of the means hereinafter fully described and particularly pointed out in the appended claims, the following description and annexed drawing setting forth in detail certain illustrative embodiments of the invention, such disclosed means constituting, however, but a few of the various forms in which the principle of this invention may be employed.

Broadly stated, therefore, this invention comprises in a process for pickling ferrous metal which includes the steps of immersing said metal in an aqueous pickling bath of ammonium acid sulphate to yield ferrous ammonium sulphate in aqueous solution, then by a process including the steps of oxidation and raising the pH to at least 7 with an ammonia-containing fluid, thereby converting said ferrous ammonium sulphate to oxide of iron and di-ammonium sulphate, recovering di-ammonium sulphate from the resulting solution, heating said di-ammonium sulphate to convert it to ammonium acid sulphate and returning said ammonium acid sulphate to the pickling operation, the improvement which comprises separating ferrous ammonium sulphate from the aqueous solution containing said ferrous ammonium sulphate, and subjecting an aqueous solution of the ferrous ammonium sulphate thus recovered to said process including the steps of oxidation and raising the pH to at least 7 and the steps following said latter process. Stated in another way, this invention comprises in a process for pickling ferrous metals utilizing an aqueous solution of ammonium acid sulphate as the pickling agent, the improvement which comprises separating ferrous ammonium sulphate from the spent pickle liquor which has been exposed to the ferrous metal, subjecting an aqueous solution of said ferrous ammonium sulphate to a process including the steps of oxidation and raising the pH to at least 7, thereby converting said ferrous ammonium sulphate to oxide of iron and di-ammonium sulphate, recovering di-ammonium sulphate from the resulting solution, and heating said di-ammonium sulphate to convert it to ammonium acid sulphate and returning said ammonium acid sulphate to the pickling operation.

Reference may be had to my prior Patent No. 2,700,004 for details of the basic process.

Reference may also be had to the annexed flow sheet which shows in diagrammatic form steps in a process embodying the improvement of the present invention.

There is provided and diagrammatically shown a pickling tank 1 and a wash tank 2 through which is passed in a continuous manner steel strip 3. Tanks 1 and 2 are shown provided with temperature responsive control means (TRC), liquid level control means (LLC), pH responsive control means (PHRC), steam traps (ST). Such control means or other well known controls may be used, if desired. The symbols in the parentheses have the same meaning elsewhere in the drawing and need not be referred to in greater detail as their significance is well understood by those skilled in the art.

Spent pickle liquor from tank 1 is pumped (4) to a settling tank 5 where solid particles and other insoluble contaminants are separated. The spent pickle liquor is then pumped through a filter 7 and then into the crystallizer 8.

Vacuum means 9 and cooling means 10 cooperate to precipitate crystalline ferrous ammonium sulphate by simultaneous concentration and cooling. This step represents one embodiment of the improvement over the prior process.

Any suitable means for causing the crystallization of ferrous ammonium sulphate from the spent pickle liquor solution may be employed, the improvement being in the separation of the ferrous ammonium sulphate rather than the specific means of accomplishing that result. Under one separation means, the hot pickle liquor is flashed into a vacuum evaporator where due to the rapid evaporation the temperature of the solution is dropped to about room temperature. This is a sufficient temperature depression and concentration effect to cause the ferrous ammonium sulphate to crystallize from the ammonium acid sulphate solution, which was, for example, a 30%-40% solution in water. Higher temperatures will yield a lower degree of separation, and lower temperature, available with higher vacuum or added cooling means, give better separation. It is desirable to reduce the temperature to at least about 30° C. for most economical operation.

A slurry of crystals is withdrawn from the crystallizer 8 and pumped 11 to a centrifuge, e. g., a solid bowl centrifuge 12, where the liquor and crystals are separated. The liquor is composed mainly of unreacted ammonium acid sulphate and ferrous ammonium sulphate in aqueous solution. The crystallization step is not capable of removing all the ferrous ammonium sulphate from solution, although the separation is remarkably complete.

This liquor is pumped 13 through a flow responsive control means (FRC) into a make-up tank 14. The crystalline ferrous ammonium sulphate is then re-dissolved in water in a dissolving tank 15. Spent wash water from the wash tank 2 may be used in part or wholly for this operation. The aqueous ferrous ammonium sulphate solution desirably containing as little water as necessary to maintain solution and also desirably elevated in temperature, is pumped to a tail gas scrubber 16 and from there it flows into the base of a neutralizer and oxidizer column 17. Air and an ammonia-containing fluid, e. g., ammonia gas, is pumped from the storage tank 18 into the column 17 which may be fitted with heating means 19. The raising of the pH to at least 7 and the oxidation operations may be performed simultaneously or sequentially in either order. Best results are obtained when the pH adjustment precedes the oxidation step. The elevation of pH is up to from 7 to about 8.5. The effluent from the column 17 is pumped 20 through a filter 21 to remove oxide of iron.

The filtrate from filter 21 is an aqueous solution of di-ammonium sulphate. It is pumped to an ammonium sulphate evaporator 22. The concentrated slurry of crystals and liquor is fed from the evaporator 22 to a cen-

trifuge 23, filtrate being re-circulated and the crystals being conducted to a rotary drier 24. In the rotary drier 24, the temperature is less than the decomposition temperature of di-ammonium sulphate. From the drier 24 the crystals of di-ammonium sulphate pass to a decomposer 25. The products of decomposition are ammonia and ammonium acid sulphate. Molten ammonium acid sulphate is pumped to a dissolving tank 26, mixed with water and the aqueous solution mixed with liquor containing unreacted ammonium acid sulphate and ferrous ammonium sulphate in solution in make-up tank 14. This mixture is fresh pickle liquor which may be heated 27 prior to introduction into the pickling tank 1.

Prior to rotary drier 24, additional di-ammonium sulphate may be added to the system to replace that lost in handling.

Other types of equipment than those diagrammatically illustrated in the annexed drawing may be used as will be well understood by those skilled in the art. The equipment depicted is for illustrative purposes only and is not to be construed as limiting the invention to the apparatus shown. Certain elements of the depicted apparatus are not essential to the operation of the process, e. g., the tail gas scrubber 16, the rotary drier 24, etc. They contribute to an efficient process, however. Other elements will be recognized by those skilled in the art as non-essential and utilization of the procedural steps in apparatus other than that shown in the annexed drawing is contemplated hereby.

The separation of the ferrous ammonium sulphate from the spent pickle liquor enables improvement in the degree of utilization of the ammonium acid sulphate, i. e., unreacted pickling agent is not being circulated through the entire system and undergoing useless chemical reaction and decomposition. Treatment of relatively pure ferrous ammonium sulphate simplifies the handling of the materials and improves the problem of maintenance, cleaning of equipment and nature of the subsequent chemical reactions. Thus the introduction of this step not only cuts down upon the amount of evaporation otherwise necessary (a very costly unit operation), but it improves the efficiency of all subsequent chemical and physical operations performed.

It should be clearly understood that with the exception of the ferrous ammonium sulphate separation step and the necessarily added incidental operations concomitant thereto, the process is essentially the same as disclosed in my prior patent aforesaid.

Other modes of applying the principle of this invention may be employed instead of those specifically set forth above, changes being made as regards the details herein disclosed, provided the elements set forth in any of the following claims, or the equivalent of such be employed.

It is, therefore, particularly pointed out and distinctly claimed as the invention:

1. In a process for pickling ferrous metal including the steps of immersing said metal in an aqueous pickling bath of ammonium acid sulphate to yield ferrous ammonium sulphate in aqueous solution, then by a process including the steps of oxidation and raising the pH to at least 7 with an ammonia-containing fluid, thereby converting said ferrous ammonium sulphate to oxide of iron and di-ammonium sulphate, recovering di-ammonium sulphate from the resulting solution, heating said di-ammonium sulphate to convert it to ammonium acid sulphate and returning said ammonium acid sulphate to the pickling operation, the improvement which comprises separating ferrous ammonium sulphate from the spent aqueous pickling solution containing said ferrous ammonium sulphate and any unreacted ammonium acid sulphate, and subjecting a water solution of the ferrous ammonium sulphate thus recovered to said process including the steps of oxidation and raising the pH to at least 7 and the steps following said latter process as aforesaid.

2. A process in accordance with claim 1 in which the

5

steps of oxidation and raising the pH to at least 7 are performed simultaneously.

3. A process in accordance with claim 1 in which the steps of oxidation and raising the pH to at least 7 are performed sequentially and in the order named.

4. A process in accordance with claim 1 in which the steps of oxidation and raising the pH to at least 7 are performed sequentially and in reverse the order named.

5. In a process for pickling ferrous metals utilizing an aqueous solution of ammonium acid sulphate as the pickling agent, the improvement which comprises separating ferrous ammonium sulphate from the spent pickle liquor which has been exposed to the ferrous metal, subjecting a water solution of said ferrous ammonium sulphate to a process including the steps of oxidation and raising the pH to at least 7 with an ammonia-containing fluid thereby converting said ferrous ammonium sulphate to oxide of iron and di-ammonium sulphate, recovering di-ammonium sulphate from the resulting solution, heating said di-ammonium sulphate to convert it to ammonium acid sulphate and returning said ammonium acid sulphate to the pickling operation.

6. A process for pickling ferrous metals which comprises the steps of immersing said metal in an aqueous pickling bath of ammonium acid sulphate to yield ferrous ammonium sulphate in aqueous solution, crystallizing ferrous ammonium sulphate from said aqueous solution, subjecting a water solution of said ferrous ammonium sulphate to a process including the steps of oxidation and raising the pH to at least 7 with an ammonia-containing fluid, thereby converting said ferrous ammonium sulphate to oxide of iron and di-ammonium sulphate, recovering di-ammonium sulphate from the resulting solution, and

6

heating said di-ammonium sulphate to convert it to ammonium acid sulphate and returning said ammonium acid sulphate to the pickling operation.

7. A process for pickling ferrous metals which comprises the steps of immersing said metal in a 35%–40% aqueous pickling bath of ammonium acid sulphate heated to a temperature of from 50° C. to 130° C. to yield an aqueous solution containing ferrous ammonium sulphate, flashing said aqueous solution containing ferrous ammonium sulphate into a reduced pressure evaporator thereby cooling and concentrating said solution and causing at least a portion of the ferrous ammonium sulphate to crystallize from solution, separating the crystallized ferrous ammonium sulphate and redissolving it in water, then by a process including the steps of oxidation with air and raising the pH to at least 7 with gaseous ammonia thereby converting said ferrous ammonium sulphate to oxide of iron and di-ammonium sulphate, filtering to remove the oxide of iron, evaporating to dryness at a temperature insufficient to decompose the di-ammonium sulphate, then decomposing the di-ammonium sulphate to convert it to ammonium acid sulphate and ammonia, admixing said ammonium acid sulphate with the mother liquor resulting from the ferrous ammonium sulphate separation step to form fresh pickling bath, adjusting the concentration of ammonium acid sulphate in the fresh pickling bath to within the range of 35% to 40%, and returning said fresh pickling bath to the pickling operation.

References Cited in the file of this patent

UNITED STATES PATENTS

2,700,004 Miller Jan. 18, 1955