G. E. HARIKE

METHOD OF PRODUCING COPPER SULFATE

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METHOD OF PRODUCING COPPER SULFATE

George E. Hartke, College Park, Ga., assignor to Tennessee Copper Company, New York, N.Y., a corporation of New Jersey

Application February 24, 1948, Serial No. 608,141

1 Claims. (Cl. 23—125)

The present invention relates to improvements in the production of copper sulphate from metal in which the reaction may be made continuous and more rapid, and in which the production will be free from loss of copper in the usual side reactions. This application is a continuation in part of my prior application Serial No. 608,141, filed August 1, 1945.

The reaction between metallic copper and sulphuric acid is slow at atmospheric temperature even in the presence of oxygen. At higher temperatures the reaction becomes practical and is usually applied at temperatures between 150° F. and 200° F. However, at these higher temperatures the presence of oxygen is not only needed for the formation of copper sulphate but also for the prevention of the formation of copper sulphide. The oxygen is usually obtained from air. Copper sulphate is a product of economic importance and much work has been done in the past to improve the method by which it is manufactured. The use of foreign catalysts such as ozone with air, the use of increased oxygen concentration by enrichment of air with oxygen or by carrying out the reaction at super atmospheric pressures, the use of methods that alternately oxidize the copper and then dissolve the oxide, are some of the improvements heretofore proposed. However, these methods involve an increase in the means and material necessary for carrying out the reaction. My invention avoids the use of these complicated and expensive methods.

The submersion of copper in an acid solution with the introduction of air to the bottom of the containing vessel has been disclosed. However, this broad procedure does not give improvement, due to the lack of uniform establishment of the proper phase relation between the gas, liquid and solid reactants. As stated in my previous application, there has been no such prior use that has been successful as far as I am aware.

Use of a tower containing shot copper with the introduction of solution sprayed on the top of the mass of copper and withdrawn from the bottom while air is introduced into the bottom and withdrawn from the top has heretofore been the most widely applied process. The shot copper commonly used in such processes is made by the well known practice of shotting the metal by pouring a small stream of molten metal into a mass of water, producing irregularly shaped particles the size of which can be controlled by variation in shotting practice but is usually about 1” in maximum dimension. Spherical shot are not desirable since the product is generally used as a starting material in manufacturing processes in which a large metallic surface and high porosity are desired. The temperature within the tower is usually maintained at 150° F.—210° F. by externally heating the solution or by introducing steam with the air by combinations of these with externally heated air.

The above described practice of producing copper sulphate from crude metallic copper follows the reactions indicated below:

Cu+CuSO_4→Cu_2SO_4
CuSO_4+O+H_2SO_4→2CuSO_4+H_2O

The solubility of cuprous sulphate in the sulphuric acid-copper sulphate solution is slight and chemical equilibrium is established quickly between the metallic copper and the solution. Thus the reaction between the copper and the solution is arrested unless and until the cuprous sulphate is oxidized in the second reaction to cupric sulphate. Ordinarily the oxygen is obtained from air.

As the relatively insoluble cuprous sulphate impedes the further reaction of solution on the copper, it is necessary to expedite the conversion into cupric sulphate. Hence the efficiency of this process is found to depend upon the readiness with which the cuprous sulphate can be converted into the cupric form.

It was the purpose of my invention described in application Serial No. 608,141 to improve the efficiency of this reaction and greatly increase the production of copper sulphate. The present invention further increases the production of copper sulphate while maintaining the higher efficiency and utilizing the materially greater proportion of the oxygen from the air being applied as in the case of my previous process.

As pointed out in my previous application, these results economize the heat required to effect the reaction. Where the consumption of oxygen is only partial a greater volume of air must be used. This has several definite objections. First, more heat must be applied to bring the greater volume of air up to the requisite temperature and second the greater amount of air will produce a greater quantity of water vapor which will be lost in the depleted air which is being vented. Third, larger reaction vessels and accessory equipment are needed and larger amounts of metallic copper are tied up in the process.

A still further object of the present invention is to avoid the undesirable production of copper
sulphide which has been found to occur whenever the solution is allowed to remain quiescent in contact with the copper metal. This reaction is very undesirable and is quite apt to occur at the operating temperature of 150–210° F. The copper sulphite forms a coating on the copper metal and practically stops further reaction. Some of the copper sulphite is suspended in the air, while some of it settles in the mass of copper plugging the voids in the metal. This condition necessitates the frequent removal of the copper sulphite from the copper surface as well as the sludge from the voids before further reaction can be carried out.

As in the case of my previous process, the present invention maintains a condition in which the copper shot, scrap copper or clippings of irregular shape and up to two inches in maximum dimension, are covered with a moving layer of liquor containing sulphuric acid and copper sulphate while being subjected to a current of air.

This condition is established and maintained throughout a mass of closely packed copper shot or the like so that the oxygen of the air may be brought into contact with the end of liquid copper surfaces and remains so until its passage out of the reaction chamber is permitted after it has been depleted of the greater amount of the oxygen present. Practically, the process can effectively consume from 50 to 85% of the oxygen in the air. An incident of this condition is that the air occupies the greater portion of the voids between the copper particles. This prevents local action by which the metal and liquor without air would react to form copper sulphide. Such sulphide is an inert sludge which will cover the metal surface preventing further reaction and requiring cleaning from time to time. This can be avoided and the process made continuous by maintaining the condition characteristic of my process.

In carrying out the reaction it is most desirable that the air permeate the voids, substantially filling them and establishing maximum contact with the solution covering the surface of the metal. This prevents the liquor from filling the voids or allowing the production of the sulphide. The particular condition to be avoided is the possibility of the liquor and the air following separate channels through the chamber, and this possibility is avoided by even distribution of the air over the bottom of the tower. Briefly stated, the condition most desirable for carrying out the process is a phase relation of solid copper in contact with the liquid which is in immediate contact with the air, both the liquid and the air being in motion. This phase relation is automatically established by the equipment described later, when operated as described and within the proper limits of air introduced. The proper amount of air introduced per square foot of tower cross-section is dependent on the apparent porosity of the charge of copper in the tower.

As described in my previous application, when using shot copper as ordinarily produced by another for use in manufacturing copper sulphate, and when the air is less than one cubic foot per minute per square foot of tower cross-section, the phase relation is not established uniformly. There is an excess amount of contact between the liquor and the solid with no air in the voids. If the amount of air is increased the number of voids containing no air is diminished until all of the voids contain air. This latter condition can be maintained up to the introduction of about 10 cubic feet per minute per square foot when the liquor is moving downwardly through the copper mass counter-currently to the flow of air as described in my previous application. At this point the velocity of the air begins to interfere with the flow of the solution over the surface and production is lowered due to the lack of sulphuric acid. With certain types of prepared secondary metal such as copper scrap, up to 20 cubic feet per minute per square foot of area can be introduced without interfering with the uniform movement of the liquid over the surface of the copper. However, with this higher rate good efficiencies are obtainable only in higher towers.

The present invention differs from the invention of my previous application in that the solution is supplied to the bottom of the copper mass and moves upwardly through the mass concurrently with the air. In my previous process where the solution moves downwardly counter-currently to the air, the downward flow of the solution is opposed by the upwardly flowing air and, at rates of air flow greater than the maximum stated above, is so reduced in amount that the desired phase relation described above is not uniformly established and the rate of solution of copper is lowered to such an extent that operation at air flows above these maxima is not practical. In the present process the solution and the air are supplied to the bottom of the copper mass and travel upwardly through the mass together. Hence the flow of solution is assisted by the upward movement of the air and the desired air-solution phase relation is uniformly established at rates of air flow higher than the maxima which limit the operation of the process described in application Serial No. 608,141.

The establishment of the desired phase relation at such higher rates of air flow by means of concurrent flow of solution and air increases the productive capacity of the tower. The productive capacity is directly dependent on the amount of oxygen consumed per unit volume of the tower. My previous process more than doubled the productive capacity per square foot of cross-section of the solution and tower. The present invention maintains all of the desirable features of my previous process by increasing the tower height with higher rates of air flow and this results in increased capacity per square foot of cross section. Thus the desirable results of decreased cost, maintenance, amount of accessory equipment and lower operational cost are obtained.

Using shot copper, and at the same rate of air flow below 10 cubic feet per minute and the same tower height, the results obtained with the present process are substantially equivalent to those obtained with my previous process. The following table indicates the conditions and proportions normally prevailing in the reaction sought for a tower approximately 30 square feet in cross-section and containing approximately 9 feet of copper mass. By way of explanation of this table, it is noted that in the usual commercial operation prior to my invention, some unused free acid remained in the solution so that the
copper sulphate was crystallized from the acid solution by cooling. Processes embodying the present invention can be operated in the same manner, as indicated in column A, but their great efficiency makes it economical to produce also neutral copper sulphate solutions for direct consumption in the production of other copper salts as indicated by column B.

### Table

<table>
<thead>
<tr>
<th>Solution Composition—Initial:</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO₄, gms. per liter.</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>H₂SO₄, gms. per liter.</td>
<td>100</td>
<td>88</td>
</tr>
<tr>
<td>Final—Cu, gms. per liter.</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>H₂O₂, gms. per liter.</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Temperature, ° F.</td>
<td>105</td>
<td>105</td>
</tr>
<tr>
<td>Circulating Rate, Gals. per Minute</td>
<td>150-200</td>
<td>100-200</td>
</tr>
<tr>
<td>Air Tower (Cal. C. Per Day) c. f. m. per square foot of tower cross-section</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Exit air—percent Oxygen (Av.)</td>
<td>26.7</td>
<td>26.7</td>
</tr>
<tr>
<td>Oxygen consumed:</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Percent of entering Oxygen</td>
<td>0.605</td>
<td>0.605</td>
</tr>
<tr>
<td>Production Rates (Copper Sulphate from Metal):</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Pounds per square foot of tower crossection per day</td>
<td>941</td>
<td>725</td>
</tr>
<tr>
<td>Pounds per tower (18.7 sq. ft.) per day</td>
<td>20,300</td>
<td>22,300</td>
</tr>
</tbody>
</table>

1 Note: Pounds of copper sulphate as CuSO₄ (2H₂O).

As the rate of air flow is increased, the height of the tower must also be increased in order to maintain good efficiencies. Thus at a rate of air flow of 3-10 cubic feet per minute, the tower height must be increased to about 18 feet in order to maintain the efficiency in the range of 90-100% (with regard to acid solution). In the process of my previous application, the rate of air flow can be further increased without excessive interference with the downward flow of the solution. In the present process, however, the rate of air flow can be much greater with good efficiency and increased productive capacity per square foot of cross-section. The following data indicates the results obtained at such higher rates of air flow, the efficiencies being stated with regard to acid solution. The operating conditions may be the same as in the table, except for the increased rate of air flow and for a corresponding increase in the rate of circulation of the solution to maintain the reaction temperature.

Assuming for example a rate of air flow of 35 cubic feet per minute per square foot of tower cross-section, the efficiency at the column height of 18 feet mentioned above would be about 40%. However, if the column height is increased to 24 feet, the efficiency will increase to about 50%. If the column height is increased to 45 feet, the efficiency will further increase to about 80%. Efficiencies of 90-100% will be obtained at column heights of about 90 feet.

Thus in the countercurrent process of my previous application, using the maximum rate of air flow for copper shot of 10 cubic feet per minute and a column height of about 18 feet to obtain 100% efficiency, the amount of oxygen consumed per square foot of tower cross-section will be about two cubic feet per minute, which is a direct measure of the number of pounds of copper sulphate produced. With a column height of 45 feet and a rate of air flow of 35 cubic feet per minute, the present process will consume about 5.9 cubic feet of oxygen per minute per square foot, so that the production per square foot is approximately tripled. However, there is a drop in efficiency to about 80% which is reflected principally in increased heat loss. This increased loss can be avoided by increasing the column height to about 60 feet at which the efficiency will be nearly 100% and production will be multiplied about 3½ times.

The above examples apply to shot copper and it is well known that shot copper varies in size, distribution and specific surface (surface per unit volume). Also these variations in size, distribution and specific surface are much wider in the case of copper scrap than in the case of copper shot. It will be apparent that the data given in the above examples will vary with the variations in the shot copper or copper scrap.

In the case of either shot copper or copper scrap, an air flow rate of approximately 50 cubic feet per minute per square foot of column cross-section is about the maximum that can be practically and economically used. With this rate of air flow, the efficiency at a column height of about 35 feet will be approximately 50%. However, to obtain efficiencies approaching 100%, a column height of about 100 feet would be needed. Such a height is undesirably for reasons of economy and ease of operation. Air flow rates higher than 50 cubic feet per minute, when used with practicable column heights, result in efficiencies that are too low for practical application.

The principal feature of the equipment for carrying out the process consists of a tower which may be made of masonry or other suitable material. It is important that this tower shall have a height of at least five feet and it may be much higher as indicated above. While the tower is usually lined with acid-proof material such as lead, any other means of protecting its inner surface may be used.

The process can be operated continuously by supplying fresh solution and air to the bottom of the tower so that they mix up through the copper concurrently and by working a reacting solution from the top of the tower. My invention has been illustrated by way of example on the attached drawings. Fig. 1 shows a diagram of a reaction chamber arranged for continuous concurrent operation and Figs. 2, 3 and 4 show details of the structure and location of the air jets. Figs. 5 and 6 show two other arrangements suitable for continuous concurrent operation.

In the form shown in Figs. 1-4, the solution is circulated upwardly through the mass of copper shot in the tower 1. Suitably spaced above the bottom 2 of the tower is a false bottom or grate 3. This will permit the solution to pass through but will support the copper particles down to the fines. The bottom 5 has an inlet pipe 6 through which the solution is supplied. A cover 7 is placed across the top of the tower. Through this cover the top is charged and the circulation of gases maintained. A charging hopper 8 mounted in the cover 7 permits the periodic introduction of shot copper or the like. This hopper is closed when not charging.

The shot copper or scrap copper is built up to form a column of at least five feet in height, or
to greater heights as indicated above. The size of the copper particles is such that they form a mass through which liquid may percolate or gases may rise evenly and without forming large passageways or channels.

The liquor inlet pipe 4 is connected to a tank 7 from which the liquor is delivered to the tower by a pump 5. In the circulating tank a coil or other heating means 17 is provided to maintain the desired temperature. This restores the heat lost in the tower 1 to maintain the temperature of the reactants in the tower in the range stated above. Any desired number of inlets 6 may be provided. The liquor moves upwardly through the mass of copper, being assisted by the upward flow of air as described below, and overflows through a pipe 9 which returns it to the tank 7.

A vent provided in the cover 5 is connected with the exhaust blower 10. By this means the deoxygenated air is drawn off from the tower at a regulated rate.

A blower 11 is provided and connected through the top to the inlet air pipe 12. The pipe 12 extends to approximately the level of the grate 3. At that point it is branched as shown at 13 and provided with a circulating system including the nozzles 14. The air discharged at these nozzles will only be under the hydrostatic pressure of the column of mixed liquid and air in the tower and rises throughout the mass of copper to establish the phase relation above described. The blower 11 is an air compressor which delivers air through the nozzles at the required pressure.

The heating of the solution in the tank 7 may be supplemented by heating the air introduced into the tower through the pipe 12, or if desired the total heat required may be supplied by introducing steam with the air.

The aqueous solution of copper sulphate containing the initial proportion of sulphuric acid is fed from the circulating tank 7 through the pipe 4. The solution also includes liquor from the final crystallisation operation and wash water. The liquor has a temperature of 150-210°F, preferably 185°F. This is maintained by means of steam coils 17 in the circulating tank 7. The solution is fed to the tower at whatever rate is necessary to maintain the temperature of the reaction at 180-185°F.

The concentration of the circulating solution is analyzed periodically and adjustment made when necessary by adding sulphuric acid. Wash water containing some copper sulphate is used to replace the water evaporated in the tower. When the copper content of the solution is about 100 gms./per liter, the solution in the circulating tank is pumped out and another batch started. Circulation over the tower and introduction of air into the bottom of the tower is continuous however.

Fig. 5 shows a tower 25 similar to the tower 1 but arranged for upward circulation of solution through the tower concurrently with the air. As in Figure 1, the copper particles are charged through a hopper 26 and are supported on a grate 27. Air is introduced into the bottom of the tower by means of a blower 28, pipe 29, and nozzles 30, while the liquor is led from the exhaust blower 31. The solution is stored and heated in a tank 32 from which it is withdrawn by a pump 33 and delivered through a pipe 34 to the top of the tower.

Instead of being delivered to the top of the mass of copper in the tower, however, the solution flows down to the bottom of the tower through an extension 35 of the pipe 34. This extension pipe passes down through the hot mixture of solution and air in the tower to a point below the grate 37 where the solution escapes from the pipe through an outlet opening 38, the pipe preferably having a baffle 39 at the outlet opening.

The solution rises and fills the tower to the level of the outlet 39 above the top of the mass of copper, the overflowing solution returning to the tank 32 through the return pipe 39.

Movement of air and solution thus take place concurrently in an upward direction, but the mass of copper is maintained submerged in the aerated solution and the desired phase relation is established and maintained under the conditions specified above.

In addition to the advantages mentioned above, the concurrent operation as shown in Figs. 1 and 5 also prevents fine copper particles from getting into the feed lines and circulating tank, while the upward movement of the solution tends to prevent clogging of the grate 27. The arrangement shown in Fig. 5 has the further advantage that if the circulation of solution should be stopped temporarily, the solution remains in the extension 35 of the pipe 39 is kept hot by the surrounding hot solution in the tower and thereby prevented from crystallising in the pipe.

The concurrent upward flow of solution and air also makes possible the use of the air lift principle for circulating the solution, thus eliminating the need for circulating pumps such as 8 and 32.

Fig. 6 shows such a system diagrammatically. The tower 40, bottom or grate 41, air inlet 42 and nozzle 43 may be the same as in Figs. 1–5. The tank 44 corresponds to the tanks 1 and 32, but is elevated to a point adjacent the top of the column of copper indicated at 45. Solution flows by gravity from the bottom of the tank through a pipe 46 to the bottom of the tower. If desired, this pipe can be located inside the tower as in the case of the extension pipe 35 of Fig. 5.

The solution entering the tower rises through the copper concurrently with the air from the nozzles 43. The specific gravity of the mixture of solution and air is less than that of the solution alone, and the hydrostatic head of the column of solution in the tank 44 and pipe 45 maintains the level of the lighter aerated solution in the tower above the top of the copper column, the solution returning to the tank through the pipe 47. Thus continuous circulation of solution through the tower is maintained without the use of circulating pumps.

By adhering to the process above described the reaction can be made substantially continuous as it has been found no interruption is required either for recharging, cleaning, or changing the solution.

At the same time the scrap copper or shot is completely consumed and no particular care need be exercised either in grading the initial charge or removing under-sized particles after the reaction has progressed.

The efficient use of the oxygen has several advantages among which are the marked economy in the quantity of heat required and the reduced amount of water vapor lost through the exhaust.

The fact that the reaction vessel is under no pressure above atmospheric, except that due to the mass of the reactants, simplifies the operation to a large degree. Conspicuous absence of copper sulphide as an objectionable byproduct is noted.

The process may be carried out as above indi-
dated and with a wide range of factors including concentration of solution, temperature, speed of air current and the like without departing from the invention as defined in the appended claims.

What is claimed is:

1. The method of producing copper sulphate which comprises forming a mass of copper that is substantially porous throughout by forming said mass of copper particles having a maximum dimension not greater than about two inches, maintaining said mass submerged in a 150°F-210°F aerated solution of copper sulphate and sulphuric acid, air being continuously introduced into the bottom of the mass at the rate of 1 to 50 C. F. M. per square foot of cross sectional area of the mass, the pressure of the gas above the solution being substantially atmospheric, the solution being continuously introduced to the bottom of the mass and moving upwardly therethrough with the air and being withdrawn from the top, and maintaining the reaction temperature.

2. The method of producing copper sulphate which comprises forming a mass of copper that is substantially porous throughout by forming said mass of copper particles having a maximum dimension not greater than about two inches, maintaining said mass submerged in a 150°F-210°F aerated solution of copper sulphate and sulphuric acid, air being continuously introduced into the bottom of the mass at the rate of 1 to 50 C. F. M. per square foot of cross sectional area of the mass, the pressure of the gas above the solution being substantially atmospheric, the solution being continuously introduced to the bottom of the mass and moving upwardly therethrough with the air and being withdrawn from the top, and maintaining the reaction temperature.

3. The method of producing copper sulphate which comprises continuously supplying a solution of copper sulphate and sulphuric acid to the bottom of a mass of copper that is substantially porous throughout, being formed of copper particles having a maximum dimension not greater than about two inches, aerating the solution as it moves upwardly through and in contact with the mass by introducing air into the bottom of the mass at a rate of 1 to 50 C. F. M. per square foot of cross sectional area of the mass, thereby establishing liquid layers conforming to and covering the exposed surfaces of said particles and in contact with air substantially filling the voids between said particles, the pressure of the gas above the solution being substantially atmospheric, maintaining the aerated solution at a reaction temperature between 150°F and 210°F, and withdrawing reacted solution from a point near the top of the mass.

4. The method of producing copper sulphate which comprises continuously supplying a solution of copper sulphate and sulphuric acid to the bottom of a mass of copper that is substantially porous throughout, being formed of copper particles having a maximum dimension not greater than about two inches, aerating the solution as it moves upwardly through and in contact with the mass by introducing air into the bottom of the mass at a rate of 1 to 50 C. F. M. per square foot of cross sectional area of the mass and distributing the air flow substantially uniformly over said area, thereby establishing liquid layers conforming to and covering the exposed surfaces of said particles and in contact with air substantially filling the voids between said particles, the pressure of the gas above the solution being substantially atmospheric, maintaining the mass of particles as copper is consumed in the reaction by supplying more particles to the top of the mass, maintaining the aerated solution at a reaction temperature between 150°F and 210°F, and withdrawing reacted solution from a point near the top of the mass.

GEORGE E. HARIKE.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Date</th>
</tr>
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<tbody>
<tr>
<td>1,944,444</td>
<td>Marsh et al.</td>
<td>Jan. 23, 1934</td>
</tr>
<tr>
<td>2,163,908</td>
<td>Bagby</td>
<td>Apr. 11, 1939</td>
</tr>
</tbody>
</table>
Certificate of Correction

Patent No. 2,533,245

GEORGE E. HARIKE

December 12, 1950

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 3, line 6, for "sulphite" read "sulphide"; line 18, for "wall" read "well";

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 25th day of December, A. D. 1951.

[Seal]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.