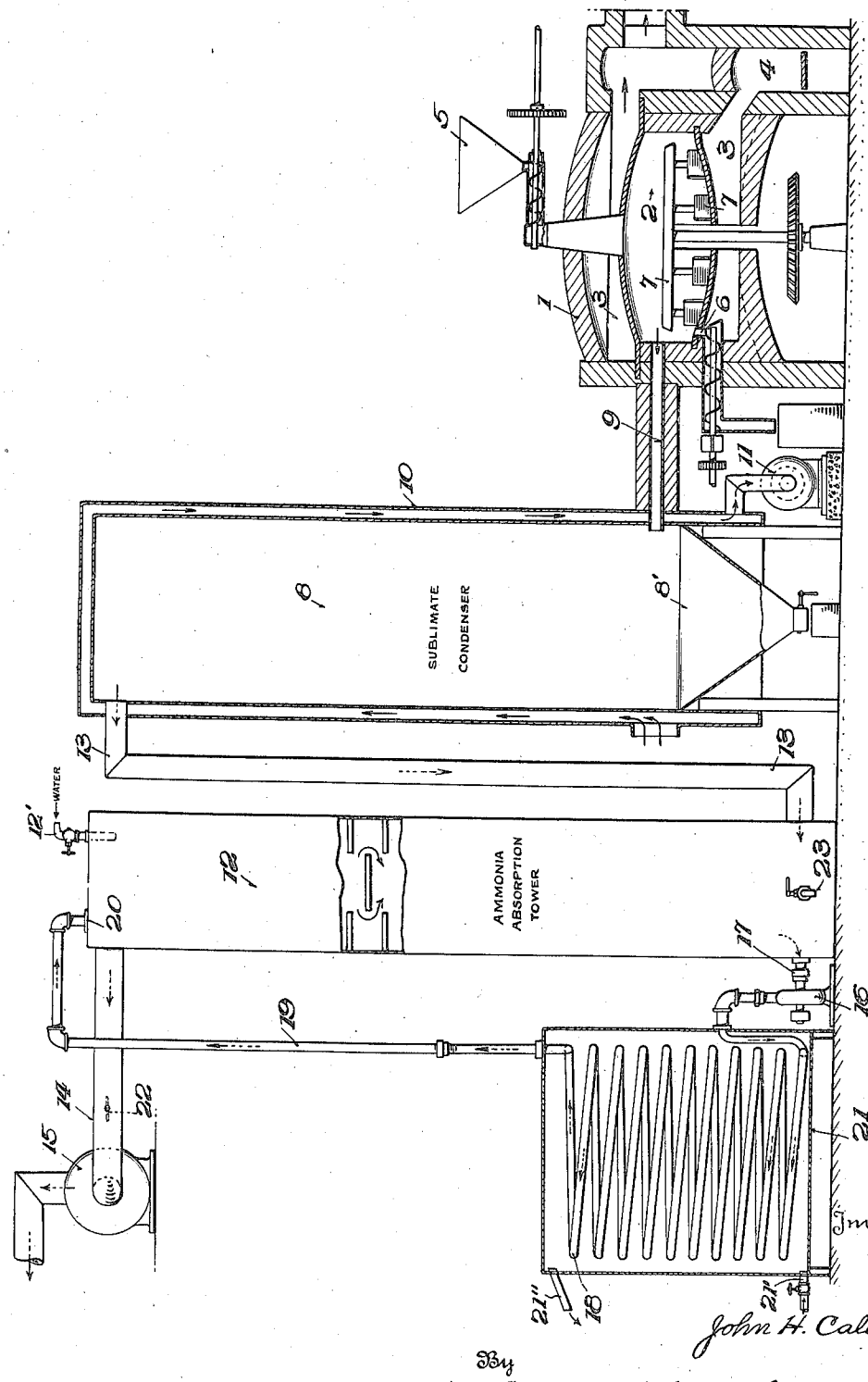
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METHOD OF PREPARING METALLIC SULPHATES FROM SULPHIDE ORES AND THE LIKE

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METHOD OF PREPARING METALLIC SULPHATES FROM SULPHIDE ORES AND THE LIKE

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This invention relates to the preparation of metallic sulphates from metallic sulphides and has as its principal object the conversion of such sulphide ores as sphalerite, galena, pyrite, etc., into corresponding sulphates. This invention is based on my discovery that if a metallic sulphide ore, such as ZnS, is heated with ammonium bisulphate, the sulphide is converted into the sulphate of the metal and the ammonium salt is reduced to the sulphite, sulphur and water according to the following equation:

$$ZnS+2NH_4HSO_4=ZnSO_4+(NH_4)_2SO_3+S+H_2O$$

I have discovered that this reaction begins at temperatures between 150° C. and 200° C., but the reaction is most rapid and the most satisfactory results are obtained at between 350° C. and 440° C., at which temperature the ammonium sulphite and sulphur are easily volatilized and may be condensed and collected by appropriate means. It is not necessary to use temperatures as high as 440° C., which is the boiling point of sulphur, for the reason that the sulphur is somewhat volatile in the ammonium sulphite and at 350° C., all the sulphur will pass over with the ammonium sulphate. I am aware of the fact that ammonium sulphite is probably dissociated in the vapor phase and is in reality only a mixture of NH_3 gas and SO_2 gas and water vapor, but throughout the description I shall refer to the ammonium sulphite as if it were completely volatile as such in order to obtain clarity and brevity.

The invention has for its further object the control of the above described reaction so as not only to obtain complete sulphation of the metallic sulphide but also to obtain economy in the use of ammonium sulphate, and further, to obtain the volatile products driven off during the reaction in a condition in which they may be readily marketed or used. The method of the invention is particularly adapted to the production of the water soluble sulphates, such as copper and zinc, which are used extensively in hydrometallurgical and electrometallurgical processes as well as having an extensive market in the form of sulphates.

The volatile products driven off may be completely recovered either as a mixture of sulphur, ammonium sulphite and ammonium thiosulphate together, or separately in the form of elemental sulphur or brimstone and ammonium sulphite. By taking special precautions, the volatile products may be recovered wholly as ammonium thiosulphate which may be used as an anticolor in industry or which may be used in the manufacture of zinc sulphide pigment, according to the method outlined in my copending application, Serial No. 688,413.

In order to describe the invention in detail, the treatment of zinc sulphide ore will be given as an illustration, but it will be understood that the invention is equally efficient for the treatment of other metallic sulphides for the purpose of preparing the corresponding sulphates. Zinc sulphide concentrates are finely ground and mixed with finely ground ammonium bisulphate. The required amount of ammonium bisulphate is determined from the analysis of the zinc concentrates and should equal or slightly exceed two chemical equivalents of ammonium bisulphate for each chemical equivalent of zinc lead, iron and lime contained in the ore. This mixture is now charged into a mechanical muffle furnace, preferably of the type commonly used for producing salt cake from sodium bisulphate and common salt. The charge may be passed through the furnace continuously or it may be treated as a batch. In the former case, the temperature should be maintained at between 350° C. and 440° C., and in the latter case, the temperature should be gradually increased until a maximum temperature of 440° C. is obtained and held there until the reaction is complete.

At the beginning of the reaction, the ammonium bisulphate fuses, forming a pasty mass, and rapid heating should be avoided at this stage to prevent rapid evolution of the volatile products from causing excessive frothing or "boiling over". Toward the end of the reaction, the charge becomes solid and, under the action of the rabbles of the furnace, is broken up so that at the end of the reaction it may be discharged from the furnace as small white grains, consisting largely of anhydrous zinc sulphate. Admixed with this will be the sulphates of iron, lead and lime corresponding to the amount of these impurities in the ore. The anhydrous zinc sulphate so prepared has a porous or sponge-like structure and dissolves very readily in water. The solution so formed may be purified of the various impurities by methods well known in the electrolytic zinc or lithopone industries.

During the heating in the muffle furnace there is a steady evolution of the volatile products, which may be collected in various well known ways, depending upon the nature of the product desired and the use to which it is to be put. It is common to collect such fume or volatile products in water and by passing these products through a spray of water in a tower or by other appropriate means all can be retained. My pre-

ferred practice, however, is based on my discovery that if the volatile products are kept free of air or other oxidizing agents and the rate of reaction be so adjusted as to produce a fume containing chemically equivalent quantities of sulphur and ammonium sulphite, then if the fume is allowed to condense in a dry tower maintained at a temperature slightly above 100° C., a sublimate is formed consisting almost entirely of ammonium thiosulphate. As far as I am aware, a sublimed or fumed ammonium thiosulphate has never before been prepared. It is well known that ammonium sulphite and sulphur react in aqueous solution to form ammonium thiosulphate, but to prepare the salt from solution, evaporation under a vacuum must be resorted to and great care taken to prevent the decomposition of the salt. But I prefer to collect the volatile products in the form of a sublimate which consists of pure white crystals of ammonium thiosulphate, and which need no further treatment in order to condition them for market.

The sublimate is best collected in a jacketed steel tower. Before the sublimation is begun, hot air is passed through the jacket of the tower to bring the temperature within the tower up slightly above 100° C. in order to prevent moisture condensing with the sublimate. As the sublimate begins to condense in the tower, the temperature rises and cold air is passed through the jacket as required to keep the temperature within the desired limits, 100° C.–150° C. I have discovered that the ammonium thiosulphate is not completely formed just as the sublimate condenses, but that some time is required for the reaction between the sublimed sulphur and the sublimed ammonium sulphite to be completed. In order that this conversion may be complete and that the final product contain a high percentage of thiosulphate and a very small percentage of uncombined sulphite, it is highly important that the fume passing into the sublimate condenser shall have exactly chemically equivalent proportions of ammonium sulphite and elemental sulphur at all times. In order that this may be accomplished, a number of very important precautions should be taken:

1. The system should be kept free of air or other oxidizing gases.

A slight positive pressure on the system consisting of the muffle and sublimate condenser will be of considerable help in this regard. For this purpose I prefer to add a little ammonium sulphate to the charge. This ammonium sulphate breaks down in the ammonia gas and ammonium bisulphate according to the following equation:

$$(2)\quad (NH_4)_2SO_4 + \text{heat} = NH_3 + NH_4HSO_4$$

The ammonia gas so generated prevents the infiltration of air and any excess of ammonia may be collected in water in tower or in an absorber connected with the sublimate condenser.

2. The rate of volatilization and the temperature must be adjusted so that the sulphur generated by Reaction (1) will pass over with the ammonium sulphite as rapidly as it is formed. Of course, if the temperature is kept at 440° C. or above, the sulphur will pass into the vapor phase as rapidly as formed and be carried over into the sublimation tower with the other gases. But if the charge is well agitated the sulphur will be taken over with the evolved gases at lower temperatures than its boiling point, and this is desirable in order to prevent the sublimation of some ammonium sulphate which is somewhat volatile at the temperature of boiling sulphur.

3. The sublimate in the tower should be maintained at a temperature of 100° C. to 150° C. in the absence of air or oxidizing gases for several hours before removal to provide sufficient time for the reaction between the sulphur and the sulphite to be completed.

In commercial operation there may be unavoidable pressure drops and under these circumstances there would be infiltration of air through cracks in the furnace. This difficulty with oxidizing gas can also be minimized by adding materials that will react with the oxygen. A method that I have used with success has been to add a certain amount of free sulphur and to substitute ammonium sulphate to produce NH_3 (Equation (2)) for part or all of the ammonium bisulphate called for in Equation (1). The sulphur reacts with the oxygen to form SO_2 and this SO_2 reacts with free ammonia and excess elemental sulphur to form ammonium thiosulphate.

If these precautions are taken the sublimate collecting on the walls and in the hopper of the tower will consist of between 90% and 99% ammonium thiosulphate in the form of a dry snow white cake which is easily removed and packed in containers.

The preparation of the ammonium bisulphate employed may be by the well known method of boiling ammonium sulphate in a pot or kettle until the free ammonia is boiled off, according to Reaction (2). The molten mass of NH_4HSO_4 may be cooled in pans or "flaked" and the solid bisulphate pulverized and is ready for charging with the sulphide ore. However, I have found it more convenient to charge the ammonium sulphate into the mechanical furnace with the sulphide ore and allow both Reactions (1) and (2) to take place together. Combining the two equations, we obtain the following, which represents the reaction between a metallic sulphide and ammonium sulphate.

$$(3)\quad 2(NH_4)_2SO_4 + ZnS = ZnSO_4 + (NH_4)_2SO_3 + S + 2NH_3 + H_2O$$

This reaction goes forward rapidly at a temperature of between 350° C. and 400° C. The zinc sulphate remains in the furnace, the ammonium sulphite and sulphur are collected in a sublimate condenser maintained at a temperature of 100° C.–150° C., and the ammonia gas and water vapor pass on into a second tower in which cold water is circulated and all the ammonia gas is recovered in the form of aqua-ammonia.

The accompanying drawing illustrates an apparatus for use in the practice of this invention. In said drawing, 1 indicates a mechanical furnace consisting of a muffle section 2 surrounded by flues 3 through which hot gases from the fire box 4 circulate. The muffle section 2 is provided with a feed hopper 5, by means of which the material to be treated is supplied to the muffle section 2, and a discharge pipe 6 and a suitable raking device 7. A sublimate condenser 8 is connected to the muffle section 2 by a pipe 9, and said tower is provided with a jacket 10 through which hot or cold air, as may be required, is circulated by means of a fan 11 to regulate the temperature within the tower. An ammonia absorption tower 12 is connected to the sublimate condenser 8 by a pipe 13. The tower 12 is partially filled

with water through the valved inlet 12'. This tower 12 is open to the air through a pipe 14 and fan 15 which discharges to the open air. Provision is made to circulate the water through the tower 12 by means of a pump 16 which takes water from the bottom of the tower through pipe 17 and passes it through the cooling coil 18 and pipe 19 and delivers it into the top of the tower at 20. The coil 18 is located in a tank 21 through which cold water or other cooling media may be circulated, entering through pipe 21' and passing out through pipe 21''. Flow of gas through the system is regulated by a damper 22 in the pipe 14.

An example of a typical continuous operation is as follows:

A charge is prepared by mixing 350 pounds fine flotation zinc concentrates, 800 pounds commercial ammonium sulphate and 20 pounds pulverized sulphur. The furnace is maintained at a temperature of from 350° C. to 440° C., and the temperature of the sublimate condenser 8 is brought to slightly above 100° C., and the circulation in the ammonia absorption tower is started by turning on the pump 16. The charge consisting of the mixture just described is then fed into the furnace at the proper rate. The fumes of ammonium sulphite, ammonia, water and sulphur begin to pass off at once into the towers 8 and 12. The sulphur and ammonium sulphite condense together in the sublimate condenser 8, and the ammonia gas passes on into the absorption tower 12 where it is dissolved in the cold water. In a short time, the temperature in the sublimate condenser begins to rise and a current of cold air is circulated in the jacket 10 of the sublimate condenser at the proper rate to keep the temperature below 150° C. but above 100° C. The ammonia gas dissolves in the water of the absorption tower 12 with the evolution of heat, and this heat is dissipated by passing the water from the tower 12 through the cooling coils 18. As the deposit of sublimate grows in the tower 8, it falls from the walls and collects in a suitable hopper 8' at the bottom of the tower. Occasional rapping on the walls of the tower 8 may be necessary to prevent the deposit on the walls from becoming so thick as to prevent the dissipation of the heat through the walls. The sublimate may be removed from the hopper at the lower part of the tower from time to time as required, care being taken to admit as little air as possible in the operation. As the concentration of ammonia in solution in the absorption tower 12 builds up to a commercial concentration, the solution is removed through any suitable discharge opening, as for example, a spigot 23, and the solution thus removed from the tower is replaced with water. The movement of the rakes in the muffle section 2 of the furnace slowly works the charge from the center outward to the periphery whence the non-volatilized part is discharged through the pipe 6. The rate of feed of the charge to the furnace should be so adjusted that this discharge consists only of zinc sulphate and the gangue constituents of the ore, such as silica, calcium, sulphate, etc. The zinc sulphate thus discharged is anhydrous and porous and dissolves readily in water with the evolution of heat, and this water solution may be purified by well known methods, such as are commonly used in purifying zinc sulphate liquors. The dry ammonium thiosulphate sublimate discharged from the sublimate condenser 8 may be marketed in the form in which it leaves said tower, or it may be dissolved in water to make the dense ammonium thiosulphate liquor required for the manufacture of zinc sulphide. The ammonia water solution withdrawn from the tower 12 may be used as a base in the zinc sulphide process of my application Serial No. 688,413, or it may be marketed as aqua-ammonia.

In case it is desired to separate the sulphur fume from the ammonium sulphite fume, this can be done by using two sublimate condensers, similar to the tower 8, the two towers being connected in tandem. In this case the first tower should be maintained at a temperature between 200° C. and 350° C. and the second chamber below 200° C. In this case a sublimate collects in the first chamber consisting almost entirely of elemental sulphur and in the second tower a sublimate collects consisting almost entirely of ammonium sulphite.

It is not essential to collect the ammonium thiosulphate as a dry sublimate but it may be collected in water to form an aqueous solution. To do this it is only necessary to replace the sublimate condenser with an absorption tower similar to the tower 12. In this case the temperature of the solution should be maintained near 100° C. so that the free ammonia may be driven over into the ammonia absorption apparatus.

It will be apparent to those skilled in the art that certain modifications and variations of the process, as illustrated in the foregoing example, may be practiced without departing from the spirit of the invention as defined in the appended claims, and such modifications and departures as fall within the terms of said claims are intended to be covered thereby.

What is claimed is:

1. In a method of preparing a metallic sulphate from the corresponding metallic sulphide, the step which consists in calcining the sulphide with an ammonium sulphate at a temperature sufficiently high to volatilize all reaction products except the sulphates.

2. In a method of preparing a metallic sulphate from the corresponding metallic sulphide, the step which consists in calcining the sulphide with an ammonium sulphate at a temperature sufficiently high to volatilize the ammonium reaction products but not high enough to appreciably volatilize the ammonium bi-sulphate or decompose metallic sulphate.

3. In a method of preparing anhydrous zinc sulphate from zinc sulphide ore, the step which consists in calcining the zinc sulphide ore with ammonium sulphate at a temperature sufficiently high to volatilize the ammonium reaction products but not high enough to appreciably decompose zinc sulphate.

4. In a method of preparing anhydrous zinc sulphate and ammonium sulphite the step which consists in calcining zinc sulphide ore with two chemical equivalents of ammonium bisulphate in the absence of oxygen and at a temperature high enough to volatilize ammonium sulphite but not high enough to volatilize ammonium bi-sulphate.

5. The method of preparing zinc sulphate, ammonium sulphite and sulphur in substantially equivalent quantities which comprises calcining a zinc sulphide ore with two chemical equivalents of ammonium bisulphate in the absence of oxygen and at a temperature high enough to volatilize ammonium sulphite and sulphur but not high enough to decompose zinc sulphate, and collecting the volatile products.

6. The method of preparing anhydrous zinc sulphate, ammonium sulphite, sulphur and am-

monia in substantially chemically equivalent quantities, which comprises calcining zinc sulphide with twice the chemical equivalent quantity of ammonium sulphate in the absence of oxygen and at a temperature between 150° C. and 440° C., and passing the volatile products first through a tower heated slightly above 100° C. to collect the ammonium sulphite and sulphur and then passing the remaining volatile products from the tower through cold water to collect the ammonia.

7. A method of preparing ammonium sulphite which comprises calcining a metallic sulphide with an ammonium sulphate at a temperature high enough to volatilize ammonium sulphite, but not high enough to volatilize ammonium bi-sulphate nor decompose the metallic sulphate formed, and collecting the ammonium sulphite.

8. A method of preparing ammonium sulphite and sulphur in chemically equivalent proportions for the purpose of preparing ammonium thiosulphate, which comprises calcining a metallic sulphide with two chemical equivalents of ammonium sulphate in the absence of oxygen at a temperature high enough to volatilize ammonium sulphite and sulphur but not high enough to volatilize ammonium bisulphate, and condensing the resulting ammonium sulphite and sulphur fumes together in a dry chamber at a temperature slightly above 100° C.

9. A method of preparing anhydrous ammonium thiosulphate which comprises calcining zinc sulphide with twice the chemical equivalent quantity of ammonium sulphate at a temperature between 150° C. and 440° C. in the absence of oxygen, condensing from the resulting volatile products a mixture of ammonium sulphite and sulphur in chemically equivalent quantities at a temperature above 100° C. and holding the resulting sublimate at that temperature until substantially all the ammonium sulphite has been converted into ammonium thiosulphate.

10. A method of preparing ammonium thiosulphate which comprises calcining zinc sulphide with twice the chemically equivalent quantities of ammonium bisulphate at a temperature between 150° C. and 440° C. in the absence of oxygen, sublimating the ammonium compounds and leaving a calcine of anhydrous zinc sulphate, then collecting the sublimates of sulphur and ammonium sulphite and converting them to ammonium thiosulphate.

11. A non-aqueous method of preparing ammonium thiosulphate, which includes subliming ammonium sulphite and sulphur in chemically equivalent proportions and condensing at a temperature above 100° C. and maintaining the sublimates at that temperature until substantially all the sulphite has reacted with the sulphur to form thiosulphate.

12. A method of preparing aqueous solutions of ammonium thiosulphate comprising calcining zinc sulphide with twice its chemical equivalent quantity of ammonium sulphate in the absence of oxygen and at a temperature exceeding 150° C. but not exceeding 440° C., passing the volatile products first through water hot enough to drive off the majority of uncombined ammonia to collect the ammonium sulphite and sulphur to form the ammonium thiosulphate solution and then through water cold enough to absorb the remaining ammonia to collect the ammonia.

13. The method of recovering elemental sulphur from sulphide ores by reacting them with an ammonium sulphate in the absence of oxygen and at a temperature high enough to volatilize the resulting sulphur.

14. The method of recovering elemental sulphur from zinc sulphide ore by reacting it with an ammonium sulphate in the absence of oxygen and at a temperature high enough to volatilize the resulting sulphur.

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