

1,091,689.

Witnesses:
H. L. Allen
A. L. Fisker.

 *Inventors*
Robert B. Wolf,
Hugh K. Moore,
by Wrigley B. S. Smith, Secy
McDonoughs

UNITED STATES PATENT OFFICE.

HUGH K. MOORE AND ROBERT B. WOLF, OF BERLIN, NEW HAMPSHIRE.

METHOD OF PRODUCING SULFUR DIOXID.

1,091,689.

Specification of Letters Patent. Patented Mar. 31, 1914.

Application filed February 1, 1910. Serial No. 541,245.

To all whom it may concern:

Be it known that we, HUGH K. MOORE and ROBERT B. WOLF, both of Berlin, in the county of Coos and State of New Hampshire, have invented certain new and useful Improvements in Methods of Producing Sulfur Dioxid, of which the following is a specification.

The present invention has for its object the commercial production of sulfur dioxid in condensed or liquid form, so that it may be properly controlled, handled, transported or conducted.

In carrying out the process, we subject the sulfur bearing material to combustion, and then from the gases which result as a product of the combustion, the sulfur dioxid is separated and is converted into liquid state. We propose to utilize calcium chlorid and water as the solvent or absorbing medium for separating the sulfur dioxid from the other gases resulting from the combustion of the raw material, for the reason that it can be refrigerated to relatively low temperatures, viz. to approximately -40° F. before the solution will solidify, whereas water solidifies quickly at approximately 32° F. Moreover the addition of calcium chlorid (CaCl_2) raises the boiling point of water without appreciably raising the boiling point of sulfur dioxid dissolved therein. Hence, when the solution of calcium chlorid, water and sulfur dioxid is subjected to vacuum to liberate the sulfur dioxid, less water vapor is given off than would otherwise be the case. One of the advantages due to the liberation *in vacuo* of the sulfur dioxid from the solution is that it reduces the temperature of the solvent to an extent equal to the latent heat of volatilization of sulfur dioxid, and conversely (assuming no chemical action takes place) the absorption of the sulfur dioxid by the solvent raises the temperature thereof to an extent equal to the latent heat of liquefaction. Hence the initial refrigeration of the solvent, which we employ as a step in our process, need be sufficient merely to extract the heat conveyed to the solvent by the passage therethrough of the unabsorbed gases, and what heat is conveyed to the solvent by conduction from the atmosphere outside the casing. We reduce the temperature of the gases entering the absorbing apparatus by an exchanger, chilling them by the waste gases discharged from the absorbing apparatus, thus reclaiming,

as it were, a large part of the initial refrigeration of the solvent which would otherwise be lost. The several pieces of apparatus, which may be combined to thus produce sulfur dioxid in a liquid state, embody novel features of construction and operation which are hereinafter specifically described and which are illustrated upon the accompanying drawings.

The drawing, which illustrates one embodiment of apparatus, represents the mechanical structure in a somewhat conventional manner.

The same reference characters indicate the same parts wherever they occur.

On the drawing, 10 indicates a cylindrical rotary burner provided with tapering portions near one end and with cylindrical extensions 11 and 12. The burner has exterior flanges resting upon supporting rolls 13 affixed upon parallel shafts 14 rotated by pulleys 15. The neck or extension 12 extends into a box 17 and is surrounded by a stuffing box 18 which furnishes a bearing and prevents the escape of gas.

19 indicates a feed pipe for the raw sulfur bearing material, leading from a spiral conveyor 20, inclosed in a cylindrical casing 21 bearing a receiving hopper 22. The conveyor 20 is driven by a pulley 23.

The delivery end of the burner is mounted in a stuffing box 24 and delivers the burned material to a casing 25, which is closed save for the inlet pipe 26, through which either air or pure oxygen is supplied. The selection of air or oxygen may be determined by the nature of the substance which is burned, or may be determined by the nature of the gas which it is sought to produce. The sulfur dioxid gas, together with other gases which may be the products of combustion, are conducted from the box 17 to a cooler or coolers through a pipe 27.

The present invention provides two coolers 28 and 29 for the gases which pass from the burner and may be used alternately for the purpose of initially chilling or cooling said gases and condensing those products of combustion, including vapors of sulfur, and gases which have a vaporizing point higher than sulfur dioxid gas. Each cooler consists of a casing 30, provided with two transverse heads or partitions 32 which support and through which extend a plurality of pipes or flues 33 through which the gases pass, the chambers beyond the partitions 32

being indicated respectively at 34 and 35. The upper chambers are divided by vertical partitions 36 into inlet and outlet chambers. The pipe 27 is connected with the inlet chambers by branches controlled by valves 37. In practice, it is proposed to keep one of the valves 37 closed when the other is opened, and vice versa, thus admitting the gases to but one of the coolers at a time. The outlet chambers are provided with outlet pipes 38, connected to a common delivery pipe 39, and being provided with valves 40. The lower compartment of each cooler is surrounded by a jacket 31, and the interior of the compartment 33 is connected with the interior of the jacket by a port 31^a. The space surrounding the tubes 33 is supplied with cold water or any other appropriate cooling medium for cooling the gases which come from the burner, water from the ordinary service pipes without refrigeration being preferably used. Either cooler may be used while the other is being cleaned. The cooling liquid is conducted to the coolers by pipes 41 and is conducted away from the water jackets by return pipes 42.

To remove the sublimed sulfur from the pipes of a cooler, the valve 43 of the supply pipe 41 is closed and steam or any other heating medium may be forced into the space surrounding the tubes 33 through supply pipes 44 provided with valves 45. When the tubes become sufficiently heated by the admission of the heating medium, the sublimed sulfur dropping from the pipes 33 into the chamber 35 is discharged through an outlet 46 having a valve 47. The pipes 42 may be provided with steam traps 48.

The gases, passing from one or the other of the coolers into the pipe 39, are conducted to an absorbing apparatus containing an absorbing liquid or a solvent which will dissolve the sulfur dioxide as hereinafter explained. A pump or blower 49 may be provided in the pipe 39 between the coolers and the absorbing apparatus. The gases may, if desired, pass directly from the coolers to the pump or blower 49, or they may be conducted through a secondary cooler, condenser or absorbing apparatus 50 controlled by a valve 51. The cooler 50 would be used when the pure oxygen is introduced to the burner instead of air, for in that case it is necessary to condense and separate the sulfur trioxide resulting from the combustion, as hereinafter explained. A by-pass 52, having a valve 53, is provided in case it is desired to conduct the gases directly to the blower 49 without conducting them through the cooler 50. From the blower 49 the gases are conducted to an absorbing apparatus which comprises a casing 54 and other appliances to be described. The pipe 55, connecting the blower and the casing 54, is arranged to conduct the gases to a horizon-

tal plane as high as the top of the casing 54 before introducing the gases into the casing, the object being to prevent an overflow into the pump 49 of the liquid contained in the casing 54.

56 indicates a body of liquid in the casing 54 for absorbing the sulfur dioxide. Any preferred absorbing medium may be employed for this purpose, although for reasons hereinbefore given, we recommend and prefer an aqueous solution of calcium chloride. Since the absorbing capacity of the absorbing medium is greater when the temperature thereof is relatively low than when it is relatively high, we keep the temperature of the absorbing medium in the casing 54 as near as possible to 32° F. or lower. The cooling of the absorbing medium may be effected either within or without the casing 54, and the drawing shows a cooling apparatus within the casing and separate cooling apparatus without the casing which may be regarded as equivalents. The interior cooling apparatus consists of the connected coils 57 for the refrigerant arranged in layers supported by gratings or perforated partitions 58. The inlet 59 is controlled by a valve 60, the outlet being indicated at 61. The cooling effect of the coils 57 is obtained by forcing a refrigerant through them. The external cooling apparatus for the absorbing medium 56 includes a coil located between a pump 63 and the pipe 64 which conducts the cooling liquid to the inlet near the top of the casing 54.

One object of providing the coolers 28, 29 and 50 is to facilitate the absorption of the gases by the absorbing medium 56 by reducing the temperature of the gases as nearly as possible to 32° F. or lower. For the sake of economy, the coil 62 may be arranged out of doors in cold weather, to be cooled solely by the out-of-door temperature, but in warm weather it may be included in some commercial refrigerating apparatus.

The gases, other than sulfur dioxide, which pass with the sulfur dioxide into the bottom of the casing 54, rise to the top of the casing and pass out in a chilled or refrigerated condition through a pipe indicated at 65. To collect any sulfur dioxide gas which escapes through the pipe 65 with the other gases, a superimposed casing 66 may be provided to contain a separate body of absorbing liquid. For this purpose, the end of the pipe 65 is sealed by the absorbing liquid. The unabsorbed gases, after passing through the absorbing fluid in the casing 66, may be conducted to any desired point by a pipe 67. The compartments in the casing 54, between the perforated partitions 58, are connected by the overflow pipes 154, 155, so that the absorbing medium is conducted downward therethrough, and as a result the absorbent is strongest in sulfur dioxide in the bottom

of the compartment *c* and weakest in the top compartment *a*, thereby allowing more complete absorption through the casing. Otherwise the solution would be of the same strength in sulfur dioxide throughout, and a greater amount of sulfur dioxide would escape from the casing. The openings in the perforated partitions 58 must be small enough to prevent the absorbent from passing from one compartment to the other. The waste or unabsorbed gases are employed for the purpose of absorbing the heat of the gases entering the absorber, and are conducted to an exchanger illustrated conventionally at 103, and consisting of a casing which receives the cold waste gases from the pipe 67 and discharging them from the pipe 67'. The waste gases and the gases from the blower travel past each other in their respective conduits (the casing 103 and the pipe 67) in opposite directions.

The absorbing fluid 56, containing in solution the sulfur dioxide gas, passes from the casing 54 through a pipe 68 to a device in which the sulfur dioxide gas is liberated *in vacuo* from the absorbing medium and which is termed a gas liberator. The pipe 68, before entering the gas liberator, passes to a horizontal plane substantially 28 feet (more or less) above the top of the casing 54 so that the liberator will not be flooded with the solution. As the level of the solution in the absorbing tank is lowered, the column of solution sustained in the pipe 68 by pressure in the tank increases, and consequently the supply of the solution to the liberator is automatically controlled.

The gas liberator is indicated at 69 and consists of a closed casing containing a plurality of approximately horizontal plates 70 arranged in staggered relation, each plate terminating a short distance from one end of the casing. The absorbing liquid being deposited upon the upper plate 70 flows in the form of a thin film or layer (approximately $\frac{1}{4}$ to $\frac{1}{2}$ of an inch in thickness) over the plates 70 successively until it reaches the return pipe 71, which conducts it back to the pump 63 by which it is again forced through the cooling coil 62 and back into the casing 54. The liberation of the sulfur dioxide gas from the absorbing fluid is effected by subjecting the absorbing fluid and the gas to a vacuum within the casing 69. By reason of the vacuum within the casing 69 a larger portion of the sulfur dioxide gas is removed from the absorbing liquid, since the liquid in the casing 69 is reduced to thin films as described, while at the same time the boiling of the water in the absorbing medium is reduced. The gas, thus liberated, is conducted by a pipe 72 to a gas condenser by which it may be converted into a liquid condition before it is delivered to a receiving or a storing chamber. The gas con-

denser comprises a closed casing 73, having the pipes 74, the vertical partitions 75, the staggered horizontal partitions 76, and the partitions 77, 77', the latter dividing the space between the plates 75 and the ends of the casing into two compartments 78 and 79. The gas introduced through the pipe 72 into the casing 73 passes around the exterior of the pipes 74 and also passes back and forth around the ends of the partitions 76, and the liquefied sulfur dioxide is conducted by pipe 60 into a vacuum chamber 81. Any other type of condenser desired may be used. The liquid sulfur dioxide delivered into the chamber 81 flows through a pipe 82 to a receiving or storage tank 83, from which it may be drawn through an outlet cock 84. A basin 85 may be arranged below the cock 84 and may be provided with a filter 86 and with an outlet 87 adapted to deliver the liquid gas into portable receivers or tanks such as that indicated at 88. The storage tank 83 and likewise the pipe 82 and the vacuum chamber 81 may be surrounded by the same cooling medium which is employed in the gas condenser 73 to convert the gas into a liquid state. For this reason, the tank 83 and the pipe 82 and the chamber 81 are inclosed by outer casings indicated respectively at 89, 90 and 91. Any appropriate cooling medium and apparatus may be employed for this purpose, that shown by the drawing consisting of a gas compressor 92 and a condenser 93 connected in a circulating system including said casings. Passing through the condenser, the refrigerating gas is finally conducted by a pipe 95 back to the compressor 92, and the cycle of cooling medium is thus completed.

The vacuum, by which the sulfur dioxide gas is liberated from the absorbing fluid, may be produced by a vacuum pump such as that connected to the vacuum chamber 81 by the pipe 96, and which is of the reciprocatory type and includes two vacuum cylinders 97, 97' placed in series and containing pistons 98, 98', affixed to a piston rod 99, actuated by a third piston 100 arranged in a cylinder 101. It may be stated that care should be taken to provide a sufficient vertical length of pipe 82 greater than the height to which a column of liquid gas would be maintained by atmospheric pressure in a vacuum tube. If desired, a device 102 comprising a casing containing an absorbent may be inserted in the pipe 96 to collect whatever sulfur dioxide gas remains uncondensed and would otherwise be exhausted by the vacuum pump into the atmosphere. In case it is desired to effect the liberation of the sulfur dioxide gas from the absorbing fluid by means of heat, the vacuum pump would not be necessary.

Although the method and apparatus, now completely described, are intended primarily

for the production of liquid sulfur dioxide, a portion of said apparatus and method may, if desired, be utilized for producing sulfur trioxide, sulfur and ferric oxide in addition to sulfur dioxide. In this event, pure oxygen instead of air is introduced to the burner. The oxygen uniting with the sulfid or sulfur produces a heat so intense that if iron sulfid is used, for example, it will break up according to these equations:



with a formation of some SO_3 , due to an uneven mixture of the oxygen; or



or



These and other reactions not specified may take place all at the same time.

The gases coming from the coolers may be further cooled before going to the blower 49 by being passed through the cooler 50, the effect of which is to condense out the sulfur trioxide and the sulfur dioxide then can be conducted to the various pieces of apparatus hereinbefore described for first absorbing, then liberating, then condensing and finally storing the same in liquid condition. The by-products of this operation may also be ferric oxide or ferrous oxide, sulfur and sulfuric anhydride. If the oxygen is sufficiently pure, the gas from the blower 49 may go directly to the gas condenser 73 without passing through the absorbing apparatus and the gas liberator.

The purpose of the absorbing and liberating apparatus is to remove nitrogen and other gases which accompany the sulfur dioxide when air instead of pure oxygen is used for giving combustion. This is an important phase of the invention for the following reasons: Where the products of combustion from the burner are passed through milk of lime, but a relatively small quantity of the sulfur dioxide gas is absorbed so that the resulting solution contains substantially 2.5% of uncombined sulfur dioxide. This is due to the fact that the products of combustion comprise large quantities of nitrogen, carbon monoxide and carbon dioxide. Heretofore this relatively weak solution has been used as the acid liquor in the digesters. By cooling the gases and abstracting the sulfur dioxide in a refrigerated solvent, we separate it from the nitrogen and other waste gases, and after liberating it from the solvent, we are able to obtain it in commercial quantities at a relatively small cost, so that we are able to inject it directly into the closed digesters, with all the advantages flowing therefrom as pointed out in our co-pending application.

As a matter of detail, we desire to state that the temperature of the cooling medium

in the preliminary coolers 28 or 29 is substantially that at which the water is drawn from the river or from any usual source of supply, and it is for this reason that the action of said medium is described as cooling. This preliminarily reduces the temperature of the products of combustion at small expense. The temperature of the cooling medium in the secondary cooler 50 (when oxygen only is used to promote combustion in the burner) is substantially 14° F. more or less. The temperature of the solvent (calcium chloride solution) when introduced to the absorbing tank is substantially 32° F. more or less, and consequently we term the reduction of the temperature of the solvent, "refrigerating" it. The temperature of the refrigerant in the condenser (when sulfur dioxide gas is condensed *in vacuo*) is -90° F. more or less.

We claim:

1. The herein described method of obtaining liquid sulfur dioxide, which consists in the following steps, to wit:—passing the products of combustion containing sulfur dioxide and other gases through a solvent refrigerated to a temperature substantially 32° F. and capable of absorbing sulfur dioxide gas, extracting *in vacuo* the sulfur dioxide from the solvent, and refrigerating the extracted sulfur dioxide gas *in vacuo*, to liquefy it.

2. The herein described method of obtaining sulfur dioxide, which consists in the following steps, to wit:—burning a sulfur bearing material, passing the products of combustion therefrom through a circulating body of refrigerated solvent for the sulfur dioxide gas, distributing the solvent and the gas absorbed thereby in thin layers in a vacuum chamber, liberating the sulfur dioxide gas *in vacuo* from said thin layers, and refrigerating the liberated gas *in vacuo* to liquefy it.

3. The herein described method of obtaining sulfur dioxide gas, which consists in the following steps, to wit:—separating from the products of combustion of a sulfur bearing substance, sulfur dioxide gas by absorbing it in an aqueous calcium chloride solution while said solution is refrigerated to approximately 32° F., and then extracting *in vacuo* said gas from said refrigerated solution.

4. The herein described method of obtaining sulfur dioxide, which consists in the following steps, to wit:—circulating a body of refrigerated solvent, absorbing in said solvent in one portion of its path sulfur dioxide from the products of combustion of a sulfur-bearing material, and liberating *in vacuo* the absorbed gas from said solvent in another portion of its path.

5. The herein described method, which consists in causing a solvent continuously

to circulate from an absorbing chamber to a vacuum chamber and vice versa, refrigerating said solvent, passing products of combustion of a sulfur bearing substance through the solvent in the absorbing chamber to cause the absorption of the sulfur dioxide gas, maintaining a vacuum in the vacuum chamber and abstracting from the solvent in the last mentioned chamber the previously absorbed sulfur dioxide gas.

6. The herein described method of obtaining sulfur dioxide gas, which consists in the following steps; to wit:—burning a sulfur bearing substance, subjecting the products of combustion to the action of a solvent capable of absorbing substantially only the sulfur dioxide gas, and thereby separating it from the other gases or products of combustion, distributing the gas-laden solvent into thin layers and extracting by a vacuum the sulfur dioxide gas from said thin layers of the solvent.

7. The method of obtaining sulfur dioxide, which consists in cooling the products of combustion from burning a sulfur bearing substance, and condensing and removing the sulfur vapor and those gases having a higher volatilizing point than sulfur dioxide gas, passing the remaining gas through a refrigerated solvent, extracting the sulfur dioxide gas from said solvent *in vacuo*, and refrigerating said abstracted gas while *in vacuo* to liquefy it.

8. The herein described method, which consists in distributing a solvent containing sulfur dioxide gas into thin layers, subject-

ing said layers to a vacuum to extract the said gas therefrom, and refrigerating said gas while *in vacuo* to condense it to liquid form.

9. The herein described method of obtaining sulfur dioxide, which consists in burning a sulfur-burning material, condensing out of the products of combustion those vapors and gases having a higher vaporizing point than sulfur dioxide, abstracting sulfur dioxide from the remaining products of combustion by absorbing it in a refrigerated solvent, and abstracting said sulfur dioxide gas from said refrigerated solvent.

10. The herein described method of obtaining sulfur dioxide, which consists in burning a sulfur-burning material, condensing out of the products of combustion those vapors and gases having a higher vaporizing point than sulfur dioxide, circulating a refrigerated body of lignin solvent through an absorbing chamber and a vacuum chamber successively, passing the remaining products of combustion through the refrigerated solvent in the absorbing chamber to cause the absorption of sulfur dioxide, liberating the absorbent sulfur dioxide in the vacuum chamber, and maintaining a vacuum in said vacuum chamber.

In testimony whereof we have affixed our signatures, in presence of two witnesses.

HUGH K. MOORE.
ROBERT B. WOLF.

Witnesses:

MARCUS B. MAY,
PETER W. PEZZETTI.