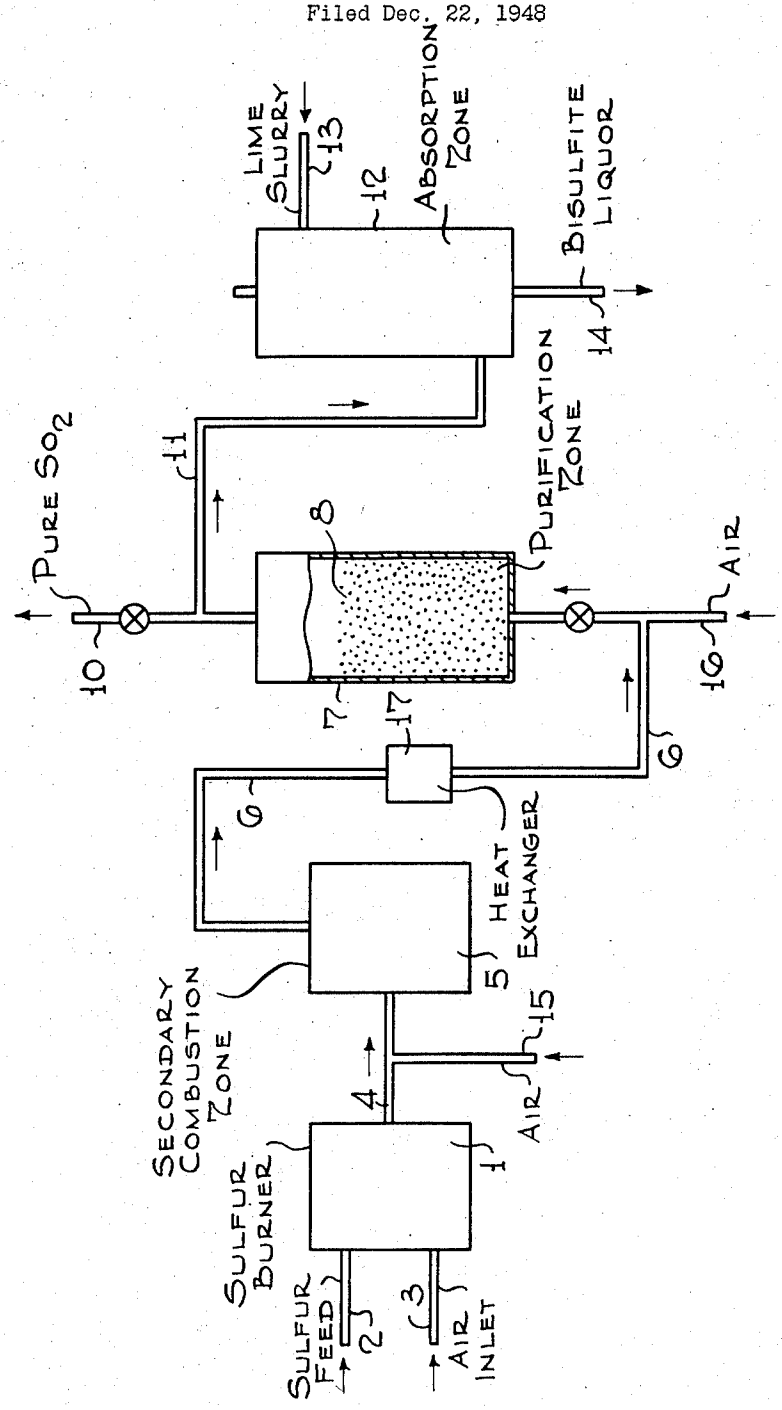
Aug. 26, 1952 W. K. LEWIS 2,608,467

PRODUCTION OF SULFUR DIOXIDE

Filed Dec. 22, 1948



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Patented Aug. 26, 1952

2,608,467

UNITED STATES PATENT OFFICE

2,608,467

PRODUCTION OF SULFUR DIOXIDE

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Application December 22, 1948, Serial No. 66,703

7 Claims. (Cl. 23—179)

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This invention is concerned with the production of sulfur dioxide and particularly the production of sulfur dioxide substantially free of sulfur trioxide, oxygen, and sulfur.

At the present time sulfur dioxide is produced by the burning of sulfur, H_2S, or sulfide ores such as iron pyrites in a sulfur burner employing air or oxygen as the oxidizing agent. The sulfur burner is ordinarily operated under conditions employing excess air. The gaseous product emerging from the burner is therefore a mixture of SO_2, SO_3, O_2, sulfur and nitrogen.

In the burning of sulfur to produce SO_2 two main problems are presented as follows:

A. How to maintain at all times the ratio of air to sulfur at the level theoretically required for complete combustion of the sulfur exclusively to SO_2, and,

B. The attainment of complete oxidation of the sulfur to SO_2.

Even if "A" were practically possible, oxidation of the sulfur would not go completely to SO_2 since some of the oxygen would be consumed in conversion of SO_2 to SO_3, some oxygen would be recovered unchanged, and some sulfur would accordingly also appear in the burner off-gas. Even if an excess of air is used complete oxidation of sulfur is not assured. An analogy exists in the combustion of coal in the operation of a steam boiler. The best modern practice is to employ about 15% excess air. However, even in the presence of such an excess of air about 0.2% to 0.3% of coal is burned to CO only. The same problem of incomplete combustion exists in the burning of sulfur.

It is oftentimes desirable to produce a sulfur dioxide gas free of contaminants such as oxygen, SO_3, and sulfur. For example, in the production of alkali or alkaline earth bisulfites used in the paper industry, a bisulfite free of sulfur and sulfate is particularly desirable. It is known that the paper industry cannot tolerate appreciable amounts of free sulfur in the SO_2 used to prepare bisulfite liquor. Therefore excess oxygen in the form of air is employed in the burner to insure its absence as far as possible. However, the use of excess air causes excessive N_2 dilution of the SO_2 and the formation of considerable amounts of SO_3. Under present practice in the production of bisulfite liquors for the paper industry, alkaline earth carbonates or hydrates are reacted with an SO_2 gas containing oxygen and SO_3. The latter impurities when present in the SO_2 consume excessive amounts of base, resulting in the formation of alkaline earth sulfate which

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is not desirable in the bisulfite solution. In addition, the presence of SO_3 gives rise to corrosion problems. Similar problems arise in the formation of alkali sulfites and bisulfites for various purposes.

This invention overcomes the above-mentioned difficulties by employing control means which act in the manner of a flywheel on the combustion zone thereby (1) compensating for deficiencies and excesses of air furnished to the combustion zone, (2) assuring statistically and on the average a supply of the theoretical amount of air thereto, and (3) assuring the absence of unburned sulfur, free oxygen and SO_3 in the final SO_2 product stream.

It is an object of this invention therefore to produce sulfur dioxide free of sulfur, oxygen and sulfur trioxide.

It is also an object of this invention to provide a continuous method for preparing such SO_2 by the burning of sulfur or sulfur-containing compounds.

It is another object of this invention to prepare sulfites and bisulfites free of sulfur, sulfates and other oxidation and reaction products.

These and other objects of the invention will be apparent from the following description of the invention.

According to this invention, pure SO_2 free of oxygen and sulfur contaminants may be continuously prepared by (1) burning sulfur, hydrogen sulfide, or sulfur-containing ores, etc., with air and/or oxygen, and (2) passing the resulting gaseous product containing SO_2 contaminated with sulfur and/or oxygen and SO_3 through a purification zone containing a mixture of Fe_3O_4 and Fe_2O_3, which, acting in the manner of a flywheel, balances out the positive or negative deviations from the theoretical in the ratio of air to sulfur supplied to the sulfur burner, preferably combined with (3) controlling the amount of air and/or oxygen fed to the burner according to the state of oxidation of the material in the purification zone. The mixture of iron oxides employed should preferably contain not substantially more than 90 weight per cent Fe_2O_3, and 10 weight per cent Fe_3O_4; or not substantially more than 90 weight per cent Fe_3O_4 and 10 weight per cent Fe_2O_3. The preferred mixture is a 50–50 weight per cent mixture of these oxides. The presence of Fe_2O_3 is necessary to assure the oxidation of any sulfur to SO_2, while the presence of Fe_3O_4 is necessary to absorb any oxygen or to decompose any SO_3. The pure oxides or ores rich in the oxides may be employed. The ma-

terial should be maintained in a dry state and preferably in a finely-divided condition. If a 50–50 weight per cent mixture of the two oxides is employed, a bed of the powdered mixture four feet deep will exert a satisfactory flywheel action of the type described above on a sulfur burner effluent containing an excess of as much as 10 per cent oxygen or sulfur even for as long as one hour to produce a satisfactory product gas.

In order to maintain the sulfur dioxide product from the sulfur burner free of O_2, SO_2, and sulfur, the amount of air or oxygen fed to the burner is controlled according to the state of oxidation of the material in the purification zone. If too high an oxidation rate of Fe_3O_4 to Fe_2O_3 is occurring in the purification zone, this is an indication of the presence of excessive amounts of O_2 and SO_3, and the amount of air to the burner is cut down. If the Fe_2O_3 in the purification zone is being too rapidly reduced to Fe_3O_4, it is an indication of the presence of excess sulfur resulting from incomplete combustion, and more air therefore is admitted to the burner.

The state of oxidation of the oxide in the purification zone may be determined: (1) by sampling and analyzing the gases which have passed through the bed of oxides in the purification zone, (2) by measuring the magnetic strength of the iron oxides present in the bed, (3) by withdrawing a portion of the iron oxides from the purification zone into a separate vessel, blowing preheated air through the withdrawn oxides to maintain satisfactory reaction and measuring the increase in temperature imparted to the air due to the exothermic heat effect of the oxidation of Fe_3O_4, or, (4) by measuring the increase in temperature of the gas after passing through the main bed of oxides in the purification zone itself.

Automatic controls either electric, magnetic or otherwise may be set up to govern the admission of air to the sulfur burner depending upon the state of oxidation of the iron oxide in the purification zone.

Reactions occurring in the purification zone are as follows:

1 $$6Fe_2O_3+S\rightarrow 4Fe_3O_4+SO_2$$

This reaction is extremely rapid even at temperatures as low as 750° C.

2 $$4Fe_3O_4+O_2\rightarrow 6Fe_2O_3$$

This reaction is rapid at temperatures in the neighborhood of 750° C. or above and proceeds smoothly even at lower temperatures.

3 $$2Fe_3O_4+SO_3\rightarrow 3Fe_2O_3+SO_2 \text{ (rapid)}$$

4 $$Fe_3O_4+5S\rightarrow 3FeS+2SO_2$$

5 $$10Fe_2O_3+FeS\rightarrow 7Fe_3O_4+SO_2$$

This reaction is rapid and quantitative. Neither SO_3 nor sulfur is formed. The reaction starts at 750° C., goes well at 800° C., and very fast at 900° C. This reaction is catalyzed by SO_2. If a reaction vessel containing a mixture of Fe_2O_3 and FeS is fluidized with SO_2, the reaction goes approximately thirty times as fast as with nitrogen at a temperature of 800° C. However, at 900° C. the reaction is very rapid even when fluidized with nitrogen.

Both reactions 4 and 5 are undesired but do occur locally at specific points in the bed. The bed must be deep enough so that reaction 5 eliminates FeS from reaction 4. Fortunately, the presence of SO_2 very greatly accelerates reaction 5.

The equations demonstrate that when excess sulfur is present the condition is remedied by reactions according to equations 1, 4 and 5. When excess oxygen or SO_3 are present, the situation is corrected by reactions according to equations 2 and 3.

FeS and Fe_3O_4 are relatively unreactive in the presence of each other and reaction apparently does not take place even at 900° C.

Unfortunately, FeS reacts with SO_2 at the temperatures required for this process to form Fe_3O_4 and elementary sulfur vapor. The reaction goes only to a small extent, but in the absence of Fe_2O_3 elementary sulfur vapor cannot be completely removed from the gas. Appreciable formation of FeS in the bed should be avoided, which is equivalent to saying that the reduction of the iron oxide should not go below the Fe_3O_4 stage.

While it is seen therefore that at one time air is supplied to the burner in excess of that required to convert the sulfur to SO_2, and at other times air is supplied in amounts insufficient to convert the sulfur to SO_2, nevertheless, it will be understood from the process outlined that, statistically, the amount of oxygen fed to the system overall is on the average the theoretical amount required to convert the sulfur to SO_2.

The manner in which the present process is carried out will be fully understood from the following description when read with reference to the accompanying drawing which is a semidiagrammatic view in sectional elevation of one type of apparatus suitable for the purpose.

Referring to the drawing, numeral **1** represents a sulfur burner in which a gas rich in SO_2 is produced. In the burner the sulfur dioxide may be made from iron pyrites, but other sources such as sulfur, hydrogen sulfide, spent oxide from gas works, and flue gases produced in ore smelting may be employed. The type of burner used varies with the material being burnt. Ordinary commercial burners may be employed. Finely divided materials demand the use of special furnaces fed with stirrers, the purpose of which is to constantly expose fresh surfaces of the burning material to the air or oxidizing agent. In this regard, numeral **2** represents a source of supply of sulfur fed to the burner while air or other gas containing oxygen is added to the burner via line **3**. The gaseous materials may pass from the burner via line **4** to a secondary clean-up zone **5** in which any unburned sulfur is removed, etc., but the necessity of such a zone is eliminated or greatly reduced by the process of this invention. The hot gaseous SO_2 containing oxygen, sulfur, and SO_3, among other impurities, is removed via line **6**. Since prior to this invention the burner has been ordinarily operated with excess air (e. g. 15% excess) in order to accomplish the most complete removal of sulfur, excess oxygen and SO_3 have always appeared in the SO_2 stream. In the practice of this invention an excess of air is fed to the burner alternately with a deficiency of air to average out to the theoretical, the flywheel action of the purification zone supplying the necessary balance. The hot SO_2 gaseous stream leaves the burner at approximately 800° C., and, if desired the temperature may be adjusted in heat exchanger **17**. The hot gaseous stream is then led into purification zone **7**. Purification zone **7** contains a bed **8** of oxides of iron, preferably a 50–50 weight per cent mixture of Fe_2O_3 and Fe_3O_4. The oxides of iron may consist of the pure oxides, ores rich in the respective iron oxides,

etc. It is sound practice to have the iron oxides mixture contain between 10% and 90% by weight of Fe_2O_3 and between 90% and 10% by weight of Fe_3O_4. It is preferable to maintain the iron oxides at a 50–50 weight per cent mixture. The temperature maintained in the bed lies between 700° and 1000° C., preferably 850° to 900° C. The thickness of the bed depends upon operating conditions. A thin bed may be employed whereby the limit thereof is uniform gas-solids contact without channeling. A thick bed may be employed, but the height of the bed is limited by the increase in pressure drop. The hot gaseous SO_2 containing the impurities described, is allowed to enter the bottom of the purification zone 7 at such a rate as will produce the so-called "fluidizing" effect in zone 7, that is, will make conditions uniform throughout the bed. The bed is fluidized in order to avoid channeling and overheating of the bed at the bottom thereof. The pressure on the bed may be substantially that employed on the burner. In the bed any oxygen or SO_3 reacts at a rapid rate with the lower iron oxide, Fe_3O_4, according to the equations previously outlined. Constant changes will occur in the composition of the iron oxide during the passage of the gas depending upon the sulfur, oxygen, and SO_3 content of the gas. As previously explained, it may be possible for the entire bed to be converted on the one extreme entirely to Fe_3O_4, and on the other extreme to Fe_2O_3. However, the state of the bed is preferably controlled to maintain at all times an iron oxide or mixture of iron oxides at least 10% by weight of which is in a state of oxidation below Fe_2O_3, and at least 10% by weight of which is in a state of oxidation above Fe_3O_4. The amount of air fed to the combustion zone is controlled, therefore, according to the state of oxidation determined in the bed. Statistically, the amount of oxygen fed to the system is on the average the theoretical amount required to convert the sulfur to SO_2. The appearance of too great a quantity of Fe_2O_3 in the bed is indicative of excessive oxidation of the iron oxide due to oxygen and SO_3 contained in the gaseous stream entering the purification zone; therefore, the amount of air being supplied to the burner is decreased in the manner outlined above so as to compensate for the excess by a corresponding air deficiency and to balance the average feed to theoretical. On the other hand, the appearance of excessive amounts of Fe_3O_4 or any iron compound of lower state of oxidation is an indication of excessive sulfur in the gaseous stream due to incomplete combustion; therefore, the amount of air fed to the combustion zone is accordingly increased. In this manner, the purification zone exerts a flywheel effect on the combustion zone.

The iron oxide in the purification zone is preferably in a finely divided condition. Material that will substantially pass through 100 mesh screen is desirable. However, material of 200 to 400 mesh may also be employed. Within the purification zone, the oxide bed is maintained in a state of turbulence by means of the fluidizing action of the gas entering the bed. In this manner, localized overheating is avoided and uniform conditions are produced throughout the bed.

Sulfur dioxide, free of oxygen, sulfur and SO_3, is removed overhead from the purification zone via line 10, after which it is cooled and stored. Nitrogen is the chief contaminant of the purified SO_2.

As previously related, the state of oxidation of the oxide in the bed in the purification zone may be determined by analysis of the gas emerging from the bed, or by measuring the temperature differential through the bed. It is also possible to draw off some of the solid from the purification zone as a side stream, blow it with air preheated sufficiently to maintain satisfactory reaction, and record the temperature rise which occurs as the exothermic heat effect of the oxidation of the Fe_3O_4. This temperature rise is indicative of the state of oxidation of the oxide present in the bed. If the oxide stream is all Fe_2O_3, no temperature rise will take place, while the highest temperature rise will occur when the stream removed is substantially all Fe_3O_4. In other words, the temperature increase will be a measure of the Fe_3O_4 content of the oxides in the purification bed. The side stream withdrawal is an excellent method of control to keep the desired ratio of Fe_2O_3 to Fe_3O_4 in the main unit. If desired, the vessel employed in the air blowing of this side stream can be enlarged in size, still serving the same purpose, but containing a considerable reservoir of oxide substantially fully oxidized to Fe_2O_3. The presence of this reservoir of Fe_2O_3 is advantageous in the event that, due to inadvertence, the oxygen content of the oxides in the main bed in the purification zone becomes so small that sulfur vapor appears in the outlet gas. The reserve bed of Fe_2O_3 in the auxiliary vessel can be employed for almost instantaneous correction of this situation. As stated bove, if the oxygen content becomes too high and oxygen appears in the outlet gas from the purification zone, one can cut down the oxygen supply to the sulfur burner to a point where it is assuredly insufficient and the situation will correct itself.

An alternative for assuring the oxidation control is that it is possible to operate the burner under constant conditions whereby excess sulfur is fed to the burner, and to control the state of oxidation in the bed of the purification zone by circulating thereto a stream of Fe_2O_3 to make up the oxygen deficiency.

At atmospheric pressure, approximately 5 sq. ft. of cross section in the fluidized purification unit are required for each ton of sulfur burned with air per day. 100 lbs. of 50–50 mixture of powdered Fe_3O_4 and Fe_2O_3 per sq. ft. will maintain the required purification for one hour in the purification zone in the presence of 10% excess sulfur or oxygen. To maintain this purification, only 3 to 5 ft. depth of bed, dense phase, is required. The bed depth to obtain satisfactory control is so shallow that particular attention should be paid to insure uniform pressure drop across the grid, and thereby maintain uniform distribution. The pressure drop through the grid should be a considerable fraction of that through the bed itself. The pressure drop through the bed can be less than 1.5 inches of mercury.

In the event that the So_2 is to be employed for the production of bisulfite liquor for use in the paper industry, the gaseous SO_2 may be withdrawn via line 11 and bubbled into a solution of calcium carbonate or a slurry of lime entering absorption zone 12 via line 13. The bisulfite liquor, free of sulfate, is removed from absorption zone 12 via line 14.

During the purification of the SO_2 stream in the vessel 7, it may be desirable to add amounts of oxygen to the gaseous stream in addition to that introduced into the stream via the com-

bustion zone. In this event, air or oxygen may be introduced into the system at various points such as through lines 15 and 16. On occasion this can be useful for correcting the temperature level of the bed. That point might also be employed for the introduction of sulfur vapor in the event that the oxidation gets out of control due to the presence of excessive oxidizing agent. However, under proper operating conditions the behavior of the iron oxide bed itself is used efficiently to control the amount of air entering the sulfur burner. When the pure SO_2 stream is employed to prepare bisulfite liquor, considerable having in calcium or other base occurs. The product is free of sulfate which would normally consume additional amounts of base material, and which is likewise undesirable in the bisulfite liquor. The presence of SO_3 normally found in the gaseous SO_2 likewise produces corrosion problems which are hereby avoided.

It will be understood that the process outlined is but one modification of the invention, and numerous modifications will occur to those skilled in the art without departing from the spirit of the invention.

For example, solid systems other than Fe_2O_3—Fe_3O_4 may be employed. However, it is necessary that the system employed possess an equivalent or better oxidation-reduction potential than the Fe_2O_3—Fe_3O_4 system. It is essential that there be used a solid phase capable of oxidation by O_2 or SO_3 to a second solid phase which in turn is capable of reduction by sulfur to the first solid phase, the oxidation-reduction potentials of the two solids in combination being such that reduction of SO_3 or O_2 by the first solid and oxidation of S to SO_2 by the second solid are both substantially quantitative. Other suitable systems are copper oxide-copper; MnO and its air oxidation products at the temperature level in question; certain spinels; molten salts, etc. Mixtures of agents thus described function satisfactorily. The copper oxide-copper system is not preferred since it requires a fluidizing carrier such as silica gel. Also, during a period of insufficient air supply, it tends to accumulate sulful in the bed, thereby converting the copper to copper sulfide. Due to the presence of the carrier a substantially higher pressure drop is required for the same protective capacity.

It should be noted that even the system Fe_3O_4—FeS may be employed if one can tolerate an SO_2 gas containing about 1% to 2% of sulfur vapor. However, the system does not quite possess the necessary oxidation potentials to oxidize the sulfur sufficiently quantitatively to produce an SO_2 stream entirely free of sulfur.

While separate zones have been described for the SO_2 production and purification, certain advantages may be achieved by employing the purification zone simultaneously as a sulfur burner by supplying sulfur and oxygen to the purification zone.

Having outlined the invention in a manner that it may be carried out by those skilled in the art, what is claimed as new and useful is:

1. A process for the continuous production of sulfur dioxide substantially free of sulfur, oxygen, and sulfur trioxide, which comprises continuously burning sulfur in a combustion zone with an oxygen-containing gas, whereby a gaseous mixture of sulfur dioxide containing at least one impurity selected from the group consisting of sulfur, oxygen, and sulfur trioxide is produced, passing the impure gaseous sulfur dioxide into a purification zone containing finely-divided iron oxide at least 10 per cent by weight of which is in a state of oxidation of Fe_2O_3, and at least 10 per cent by weight of which is in a state of oxidation of Fe_3O_4, maintaining a temperature of 700° C. to 1000° C. in the purification zone, controlling the amount of an oxygen-containing gas fed to the combustion zone to maintain the iron oxide in the purification zone in said required state of oxidation and recovering from the purification zone gaseous sulfur dioxide substantially free of sulfur, oxygen, and sulfur trioxide.

2. A process according to claim 1 in which the iron oxide bed is a bed containing 50 weight per cent Fe_2O_3 and 50 weight per cent Fe_3O_4, and in which the oxygen-containing gas is supplied to the combustion zone in the form of air.

3. A process for the continuous production of sulfur dioxide substantially free of sulfur, oxygen, and sulfur trioxide, which comprises burning hydrogen sulfide in a combustion zone with an oxygen-containing gas, whereby a gaseous mixture of sulfur dioxide containing at least one impurity selected from the group consisting of sulfur, hydrogen sulfide, oxygen, and sulfur trioxide is produced, passing the impure gaseous sulfur dioxide into a purification zone containing finely-divided iron oxide, at least 10 per cent by weight of which is in a state of oxidation below Fe_2O_3, and at least 10 per cent by weight of which is in a state of oxidation above Fe_3O_4, maintaining a temperature of 700° C. to 1000° C. in the purification zone, controlling the amount of an oxygen-containing gas fed to the combustion zone to maintain the iron oxide in the purification zone in said required state of oxidation and recovering from the purification zone gaseous sulfur dioxide substantially free of sulfur, hydrogen sulfide, oxygen, and sulfur trioxide.

4. A process according to claim 3 in which the iron oxide bed is a bed containing 50 weight per cent Fe_2O_3 and 50 weight per cent Fe_3O_4, and in which the oxygen-containing gas is supplied to the combustion zone in the form of air.

5. A process for the continuous production of sulfur dioxide substantially free of sulfur, oxygen, and sulfur trioxide, which comprises continuously burning iron pyrites in a combustion zone with an oxygen-containing gas, whereby a gaseous mixture of sulfur dioxide containing at least one impurity selected from the group consisting of sulfur, oxygen, and sulfur trioxide is produced, passing the impure gaseous sulfur dioxide into a purification zone containing finely-divided iron oxide at least 10 per cent by weight of which is in a state of oxidation below Fe_2O_3, and at least 10 per cent by weight of which is in a state of oxidation above Fe_3O_4, maintaining a temperature of 700° C. to 1000° C. in the purification zone, controlling the amount of an oxygen-containing gas fed to the combustion zone to maintain the iron oxide in said purification zone in the required state of oxidation and recovering from the purification zone gaseous sulfur dioxide substantially free of sulfur, oxygen, and sulfur trioxide.

6. A process according to claim 5 in which the bed of iron oxide is a bed containing 50 weight per cent Fe_2O_3 and 50 weight per cent Fe_3O_4, and in which the oxygen-containing gas is supplied to the combustion zone in the form of air.

7. A process for the production of sulfur dioxide substantially free of sulfur, oxygen and sulfur trioxide which comprises burning a sulfur-

containing material in a combustion zone with an oxygen-containing gas whereby a gaseous mixture of sulfur dioxide containing at least one impurity selected from the group consisting of sulfur, oxygen, and sulfur trioxide is produced, passing the impure gaseous sulfur dioxide into a purification zone containing finely divided iron oxide, at least 10% by weight of which is in a state of oxidation of Fe_2O_3, and at least 10% by weight of which is in the state of oxidation of Fe_3O_4, maintaining a temperature of 700° C. to 1000° C. in the purification zone, controlling the amount of oxygen-containing gas fed to the combustion zone to maintain the iron oxide in the purification zone in said required state of oxidation and recovering from the purification zone gaseous sulfur dioxide substantially free of sulfur, oxygen, and sulfur trioxide.

WARREN K. LEWIS.

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