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R. KNIETSCH.

PROCESS OF PURIFYING BURNER GASES.

APPLICATION FILED AUG. 5, 1898.

Fig.1

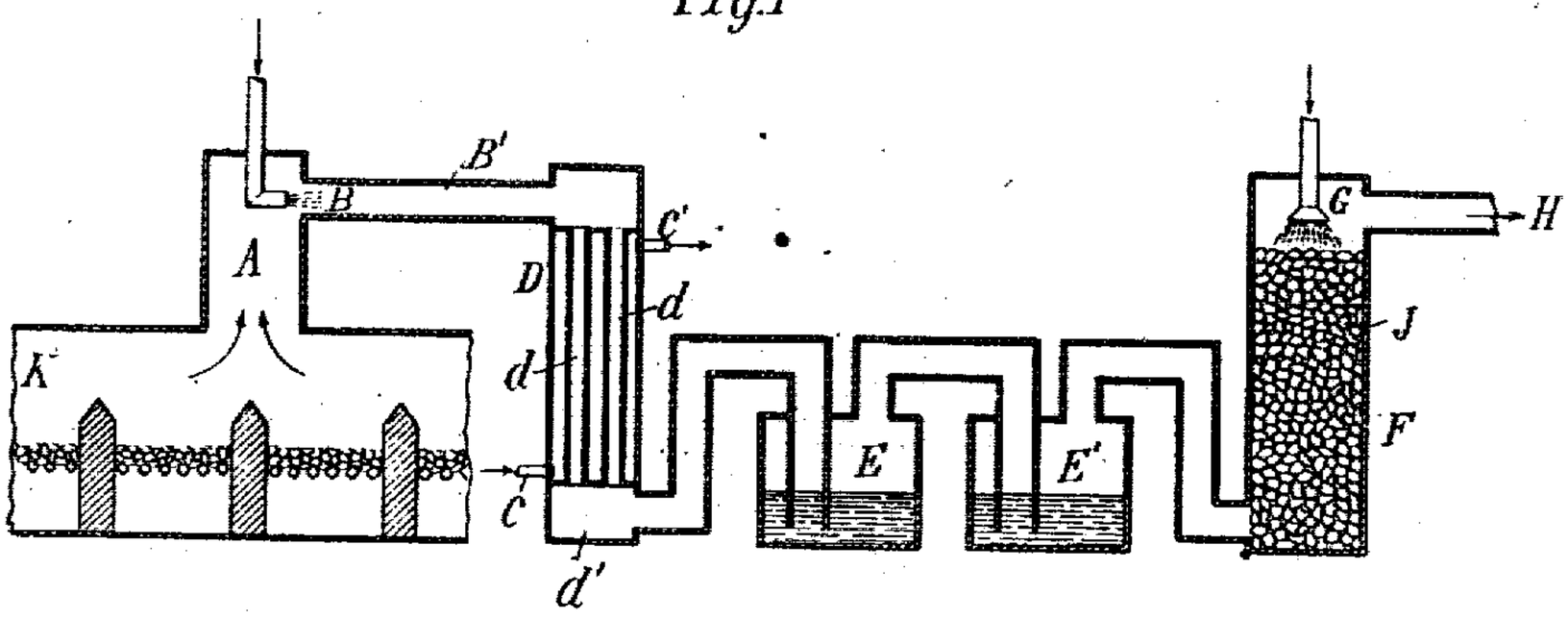


Fig.2

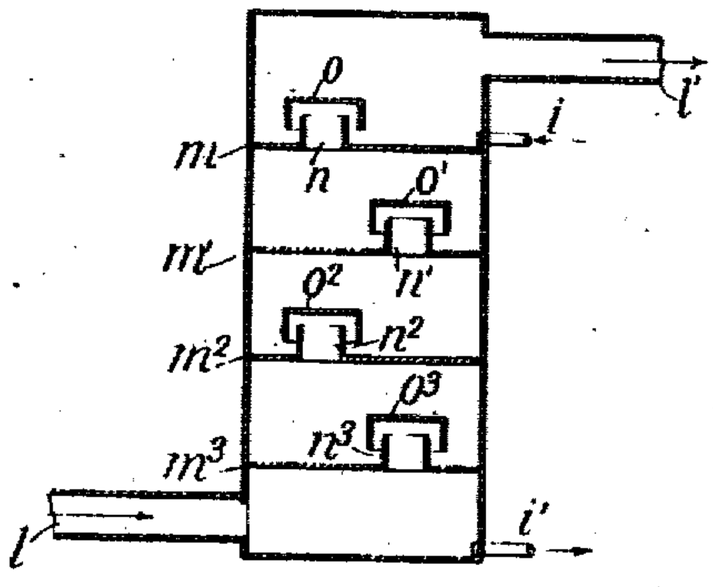
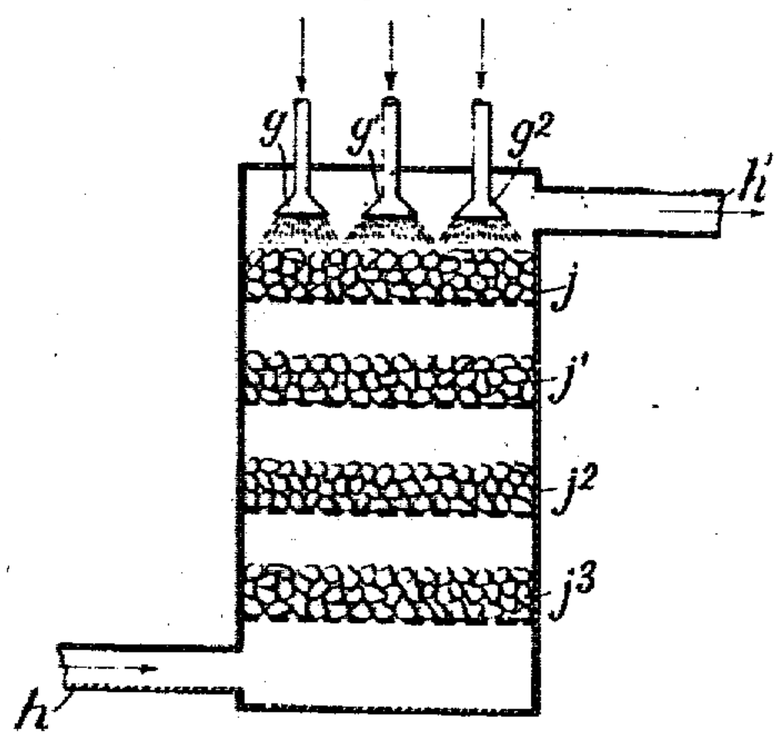


Fig.3



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UNITED STATES PATENT OFFICE.

RUDOLPH KNIETSCH, OF LUDWIGSHAFEN-ON-THE-RHINE, GERMANY, ASSIGNOR, BY MESNE ASSIGNMENTS, TO GENERAL CHEMICAL COMPANY, A CORPORATION OF NEW YORK.

PROCESS OF PURIFYING BURNER-GASES.

No. 822,373. Specification of Letters Patent. Patented June 5, 1906.

Application filed August 5, 1898. Serial No. 687,770.

To all whom it may concern:

Be it known that I, RUDOLPH KNIETSCH, a subject of the German Emperor, and a resident of Ludwigshafen-on-the-Rhine, Germany, have invented a certain new and useful Process of Purifying Burner-Gases, of which the following is a specification.

In my Letters Patent Nos. 652,119, 688,020, and 692,018 I have described improvements in the manufacture of sulfuric anhydrid and a new apparatus for use therein, having for its object the practically quantitative conversion of the sulfur dioxid in sulfurous-acid gases into sulfuric anhydrid by the contact process by means of the regulated cooling of the contents of the contact-chamber, so as to maintain the temperature thereof substantially between the composing and decomposing temperature of sulfuric anhydrid being formed. I have discovered that I can achieve said result continuously and invariably while supplying impure sulfur-dioxid gases to the contact material provided the impurities in such gases do not include certain substances the deleterious influence of which was first discovered by me. By the application of this discovery I can produce in said process from "burner-gases" (by which I mean such impure sulfur-dioxid gases as are produced or are similar to those produced from burning pyrites, crude sulfur, or other sulfur containing raw materials) a practically continuous approximately quantitative yield of sulfuric anhydrid with sufficient economy for general commercial application. The principal constituents of ordinary pyrites are the following elements or compounds thereof: iron, manganese, copper, nickel, arsenic, antimony, phosphorus, mercury, lead, zinc, bismuth, thallium, selenium, &c. Many of these on roasting the ores are liable to pass into the burner-gases, either free or in combination, either as dust or as gas. Even if practically pure sulfur be used as the source of SO_2, some sulfuric anhydrid is formed, and since the ore used in burning contains moisture the result is that the SO_2 produced contains sulfuric anhydrid which passes forward as a suspended mist.

Hitherto it has been supposed that the deterioration in efficiency of the contact material was due to ashes, dust, and soot, and the removal of these has been unsuccessfully attempted by mechanical purification; but I have discovered that besides these the impurities in said burner-gases, which interfere with the continuous accomplishment of said result by the contact process of my above-referred-to patents, are substantially the sulfural, arsenical, and mercurial impurities, or, in other words, sulfuric-acid mist, sulfur vapor, arsenic, mercury, and the compounds of the last two. These substances were understood to be volatile at a red heat, which is the approximate temperature at which sulfuric anhydrid was known to be composed from sulfur dioxid and oxygen, and I believe that no one, until myself, suspected that they exercised any deteriorating influence on the contact material.

My process departs from the apparently evident way of immediately passing into the contact mass the relatively dry and hot roasting-gases after having freed them from dust as far as possible. It substitutes a new and particular purification which preferably consists in the following features: first, a special treatment of the gases while hot with a jet of steam or other agitator; second, a subsequent gradual cooling; third, removal of condensed impurities; fourth, successive washings with water or sulfuric acid until sufficiently pure, as may be determined by especial tests; fifth, said tests consisting, first, of an optical test to show freedom from dust and mist, and, secondly, of a chemical analytical test to show freedom from arsenic, mercury, and their compounds; sixth, drying the gases by sulfuric acid. To achieve this purity, a jet of steam is blown into the hot gases as they emanate from the pyrites-burner. This steam produces the following effects:

First. It mixes the gases thoroughly and brings about a more perfect combustion of any sulfur or other combustible matter. This mixture and promoted combustion can also be effected with a jet of air or other combustion-promoting gas—say a portion of the purified gases ready for the contact process; but then the steam must be blown in later.

Second. I have found that it is preferable for the purpose of an easy and total washing of the roasting-gases, especially from pyrites containing much arsenic, to cool the gases not suddenly, but gradually, in suitable cooling apparatus. Since, however, all said gases con-

tain concentrated sulfuric-acid vapors which are condensed when cooling the metals of the cooling apparatus, usually consisting of iron or lead, are strongly attached, and thus the apparatus are soon deteriorated or destroyed. If, however, a quantity of steam is blown into the gases sufficient to bring down the concentration of the condensed sulfuric acid to a strength of 10° to 40° Baumé, this difficulty is overcome.

Third. When cooling the gases in the ordinary way and without treatment with steam, the solid impurities in combination with sulfuric acid quickly deposit on the inner walls of the coolers or conduits as a hard crust, which stops up the pipes and, like boiler incrustations, is difficult to remove. By blowing steam into the hot gases this formation of crusts is avoided and the said impurities form a mud which is easily collected and removed.

Fourth. Further, the addition of the steam renders it possible to more easily wash the gases subsequently and gives greater certainty of attaining the desired purity.

Fifth. Finally, the action of the steam serves to avoid the formation of volatile hydrogen compounds of the admixed impurities, especially of arsenic or its compounds, which also could be formed by the action of the concentrated sulfuric acid on the metals of the coolers and the impurities and which can be removed only with great difficulty, therefore passing into the contact mass and slowly rendering it inactive.

The gases after having been treated by steam pass on through an iron or brick work flue, in which they cool gradually, into a system of lead pipes arranged to act as a cooler. Here they are cooled down to about 100° centigrade or less. At this point the mud containing the impurities is conveniently removed from the path of further incoming gases. They are then passed into washing-towers or other washing apparatus and washed with water or dilute or concentrated sulfuric acid. If not already washed with concentrated sulfuric acid, they finally are thoroughly dried with this concentrated acid or other drying agent. The extent to which the washing must be carried out must be determined by the aid of the tests already mentioned and will depend on the nature and degree of impurity to be eliminated. This washing is best effected in a system of washing bottles or other washing apparatus set up in series, and pumping machinery is used to move the gases relatively to the washing liquid. The washing liquid will at the beginning of the operation absorb some sulfurous acid gas, but will soon become saturated, so that the sulfurous-acid gas will from that time on simply pass through the washing liquid without being further absorbed thereby. If water be the washing liquid employed, it soon becomes converted into dilute sulfuric acid. The use of concentrated sulfuric acid is not recommended in ordinary cases, because it requires considerable expenditure of power to remove it from the washing apparatus and because the said apparatus is liable to become incrusted. The washing apparatus can be constructed on the principle of the ordinary washing-bottles, so that the gase have to overcome the pressure of the liquids in them, and consequently the liquid which is in constant movement becomes intimately mixed with the gases, or the gases may be scrubbed by the energetic movement of the washing liquids through the gases. No material should be used in the washing apparatus which in the presence of the acid liquid might give rise to the production of noxious gases—for instance, arseniureted hydrogen. Sulfuric acid and any sublimates and flue-dust are precipitated in the cooler and any going over are held in the washing apparatus, and the liquid running from these is collected in lead boxes and allowed to settle. The sulfuric acid obtained in this way can be poured off from the sediment and be used as diluted sulfuric acid or it can be converted into concentrated sulfuric acid by the sulfuric anhydrid obtained by the contact process. If not already washed with concentrated sulfuric acid, the gases are finally thoroughly dried by means of such concentrated acid or other drying agent.

The extent to which the washing must be carried will depend upon the nature and amount of the impurities to be eliminated and can be determined by tests, as aforesaid. These tests are more fully described as follows: In the first place the apparatus is so arranged that a layer of the gas some yards long is illuminated by means of a lamp at one end, while from the other end the operator can look through the entire layer of gas toward the light. It is necessary that no dusty or misty admixture shall be observable. If this is demonstrated by the optical test, it is only necessary to examine the gases for such impurities as would not be shown by the optical test. Among these impurities there is in particular arseniureted hydrogen and possibly also mercury vapors. In order to detect these, a portion of the stream of the purified gas is passed for a long period—say twenty-four hours—through a wash-bottle containing distilled water, and the water so treated is then examined according to any suitable chemical analytical method. In this way any considerable traces of the dangerous impurities can be discovered.

The above description of the process applies most closely to the purification of the gases derived from the furnaces in which pyrites are burned or roasted; but gases con-

taining sulfur dioxid from other sources can be purified in a similar way. In practical working it is easy and best to effect both the above-described tests in the manner described; but of course if the chemical test alone constantly indicated the freedom of the gases from all traces of noxious impurities the optical test could be dispensed with.

In the accompanying drawings I have shown an apparatus by which my process may be successfully performed. Figure 1 thereof is a vertical diagrammatic section, and Figs. 2 and 3 are modifications of certain parts.

In Fig. 1 the pyrites-burner gas, for example, leaves the pyrites-burner K by way of the dome A, at whose exit the gas meets a jet of steam B, above referred to, and passes along and through the pipe B', in which the gas is gradually cooled, and thence into the cooler D, where it is further cooled by means of, say, a cooling liquid circulated through tower D around the gas-passages *d d* from the liquid-inlet opening *c* to the liquid-outlet openings *c'*. *d'* is a chamber or pocket for the reception and removal of impurities deposited in the cooling-tower. On leaving tower D the gas next passes through the above-referred-to washing apparatus E E' and thence into the drying-tower F, which is filled with coke J, which is sprinkled with concentrated sulfuric acid supplied through the sprinkler G. The dried gas leaves the tower F by the passage H.

Fig. 2 represents another form of washing apparatus which may be used in place of E E' of Fig. 1. The water enters the upper compartment through the pipe *i* and escapes from the lower compartment through the pipe *i'*. The gas enters through the pipe *k* and escapes through the pipe *k'*. The compartments are formed in the tower by the horizontal partitions *m*, *m'*, *m²*, and *m³*, respectively, containing the upwardly-extending nipples *n*, *n'*, *n²*, and *n³*, covered by the hoods *o o' o² o³*, so as to bring the upwardly-moving gases in intimate contact with the downwardly-moving water in the passages between said hoods and nipples.

Fig. 3 represents another form of drying-tower in which the coke is arranged in horizontal layers *j j' j² j³*, which are sprinkled with concentrated sulfuric acid entering the apparatus through the plurality of sprinklers *g g' g²*. The gas to be dried enters this drier at *h* and leaves it at *h'*

I claim—

1. In the manufacture of sulfuric anhydrid by the contact process, the process of purifying burner-gases which consists in agitating such gases while hot, and then cooling and washing the gases, and drying them.

2. In the manufacture of sulfuric anhydrid by the contact process, the process of purifying burner-gases which consists in blowing a jet of steam into said gases while they are hot to agitate them and reduce their concentration, and then cooling, washing and drying said gases.

3. In the manufacture of sulfuric anhydrid by the contact process, the process herein described of preparing burner-gases for purification, which process consists in first commingling them with aqueous vapor so as to reduce the concentration of condensed acid contained therein and then gradually cooling said gases, and thereupon removing impurities as described.

4. In the manufacture of sulfuric anhydrid by the contact process, the process of treating burner-gases which consists in removing substantially all arsenical impurity therefrom prior to conversion.

5. In the manufacture of sulfuric anhydrid by the contact process, the process of treating burner-gases which consists in removing substantially all arsenical and mercurial impurity therefrom prior to conversion.

6. In the manufacture of sulfuric anhydrid by the contact process, the process of treating burner-gases which consists in removing substantially all sulfur and arsenical impurity therefrom before conversion.

7. In the manufacture of sulfuric anhydrid by the contact process, the process of treating burner-gases which consists in removing substantially all sulfur, sulfuric acid and arsenical impurity therefrom prior to conversion.

8. In the manufacture of sulfuric anhydrid by the contact process, the process of purifying burner-gases which consists in agitating the gases in the presence of moisture and gradually cooling them, and washing the gases in a liquid saturated with sulfurous-acid gas.

9. In the manufacture of sulfuric anhydrid by the contact process, the process of purifying burner-gases which consists in agitating the gases and gradually cooling them, and washing them in a liquid saturated with sulfurous-acid gas.

10. In the manufacture of sulfuric anhydrid by the contact process, the process of protecting the contact substance which consists in separating out of the burner-gases, the arsenical impurity, substantially as and by the means described.

11. In the manufacture of sulfuric anhydrid by the contact process, the process of purifying burner-gases which consists in cooling them gradually and continuously removing solid impurities, then bringing them in contact with a liquid capable of removing liquid and gaseous impurities, and finally drying them.

12. In the manufacture of sulfuric anhydrid by the contact process, the process of treating burner-gases which consists in first cooling them gradually, then continuously removing a part of the impurities, and then passing the gases through a liquid capable of removing the remaining impurities.

In testimony whereof I have hereunto set my hand in the presence of two subscribing witnesses.

RUDOLPH KNIETSCH.

Witnesses:
GUSTAV L. LICHTENBERGER,
ADOLPH REUTLINGER.